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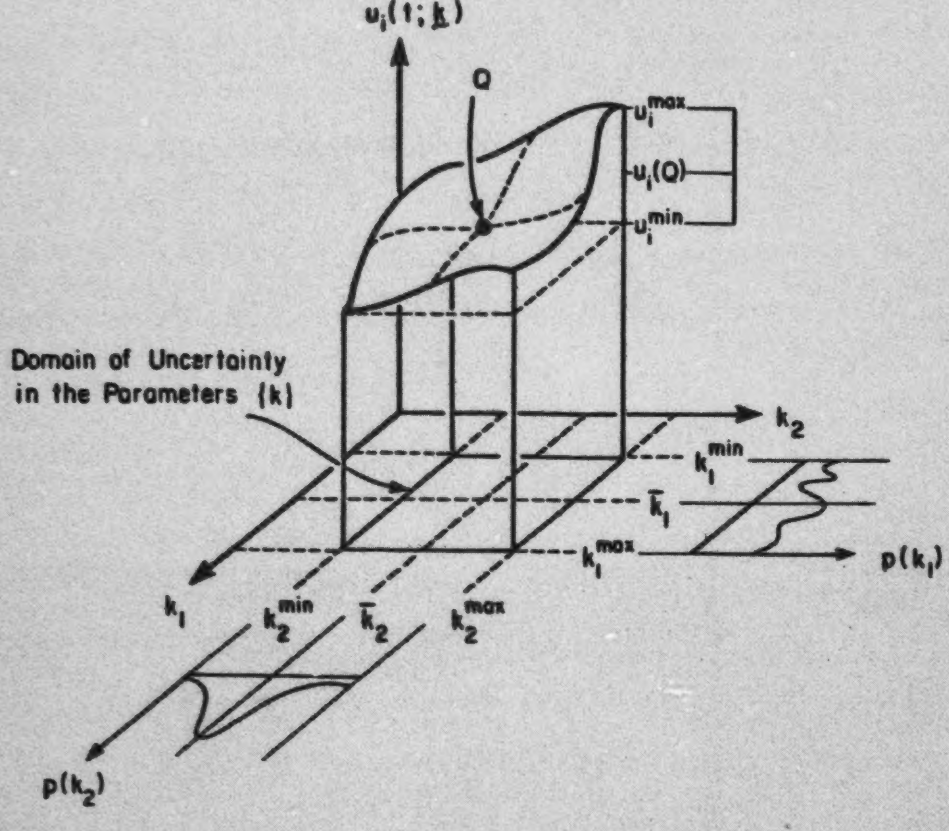
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16. ABSTRACT

The quantification of uncertainty in long-range transport model predictions and the implications of these uncertainties on formulations of control policy have been the subject of investigations by both the United States and Canada. To more fully address these topics, the American Meteorological Society (AMS) was requested to convene a workshop in September 1984 at the National Academy of Sciences Study Center in Woods Hole, Massachusetts. Joint sponsorship was provided by the U.S. Environmental Protectio Agency, the Ontario Ministry of the Environment, Canada, and the Atmospheric Environment Service of Environment Canada.

The AMS workshop was three and one-half days in duration and involved participation by 38 scientists from the United States, Canada, and Europe. Five invited draft chapters were prepared prior to the workshop to provide a focus for discussion, i.e., to raise the pertinent scientific issues to be addressed by the participants. This AMS publication contains the complete documentation of the workshop including the five invited chapters, recent developments in model evaluation and sensitivity analysis, and the reports of the Eulerian and Lagrangian working groups.

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Report prepared under the sponsorship of the U.S. Environmental Protection Agency, the Atmospheric Environmental Services Canada, and the Ontario Ministry of the Environment — Canada

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SOURCES AND EVALUATION OF UNCERTAINTY IN LONG RANGE TRANSPORT MODELS

Edited by

Kenneth L. Demerjian*[1]

A compendium of commissioned papers presented at the AMS Workshop on Sources and evaluation of uncertainty in long range transport models. Woods Hole, MA.

*This work was performed while at Harvard University as a Visiting Scientist in Energy and Environmental Policy Center and Interdisciplinary Programs in Public Health on assignment from the National Oceanic and Atmospheric Administration.

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PREFACE

It has long been recognized that pollutant emissions have the potential of being transported long distances. But it was also generally accepted that the consequences of air quality impacts due to transported pollutants from distant sources were negligible. To some extent this was justifiable given the diminished concentrations resulting from the dilution and cleansing effects air pollutants undergo during extended transport periods. One practice for the meeting of air quality standards in the United States, prior to New Source Performance Standards legislated in the Clean Air Act Amendments of 1977, had been to take advantage of dilution effects through the use of tall stacks and the placement of major emission sources in sparcely populated regions with low emission density.

With the advent of increased sophistication in monitoring air pollutants and our continued evolving knowledge of the chemical and physical dynamics of the atmosphere, it has become quite apparent that pollutants can be transported over long distances and have a significant impact on ambient air quality and other environmental media. Documented evidence on the long distance transport of photochemical oxidants, particulate sulfates, and their respective precursors as well as the pollutant-related effects of visibility degradation and acidic deposition is now available. As the complexity of the long range transport pollutant system became apparent, atmospheric transport and transformation models were developed to help provide an integrated conceptualization of the operative processes. In addition the models were also used to provide guidance on the relationships between source emissions and pollutant receptors, that is, to provide quantitative estimates of the expected change in air quality or deposition as a result of specified change in emissions.

The science of air pollutant simulation modeling plays an important role in elucidating our understanding of the complex chemical and physical interactions of anthropogenic emissions in the atmosphere as well as providing significant guidance as to the most effective strategies to mitigate air pollutant related environmental problems. It is therefore important that the scientific community monitors the progress and continues to stimulate this research field to assure that the best science and methodologies are brought to bear on the problem.

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To this end, the American Meteorological Society (AMS), under sponsorship from the U.S. Environmental Protection Agency, the Atmospheric Environmental Service, Canada and the Ontario Ministry of the Environment, Canada, convened a workshop in September 1984 to address one aspect of long range transport modeling which has been a topic of considerable concern, "the quantification of uncertainty in long range transport (LRT) model predictions".

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INTRODUCTION

In February of 1984 the American Meteorological Society convened a workshop steering committee under the chair of Dr. Kenneth L. Demerjian to discuss a propectus for a workshop on the "Sources and Evaluation of Uncertainty in Long Range Transport Models". The steering committee participants included: Dr. Len Barrie, Dr. Al Christie, Dr. Douglas Fox, Dr. P.K. Misra, Dr. Philip Roth, Mr. Frank Schiermeier, Dr. Akula Venkatram, and Dr. Fred White. The steering committee developed the scope, format and objectives for the workshop as well as prepare a list of potential participants. As a result of the steering committee's deliberations a workshop was convened at the National Academy of Sciences Study Center in Woods Hole, Massachusetts on September 18-21, 1984.

The workshop which was 3 1/2 days in duration, had participation from 38 invited national and international experts. The participants were as follows: Dr. Len Barrie, Atmospheric Environment Service; Dr. Bruce Beck, Imperial College of Science & Technology; Dr. Chandrakant Bhumralkar, SRI International; Dr. Gregory Carmichael, University of Iowa; Dr. Julius Chang, National Center for Atmospheric Research; Dr. Han-Ru Cho, University of Toronto; Dr. Al Christie, Atmospheric Environment Service; Mr. Terry L. Clark, NOAA/MD ASRL; Dr. Kenneth L. Demerjian, Harvard University; Mr. Roland Draxler, NOAA/ARL; Dr. Anton Eliassen, Norwegian Meteorological Institute; Dr. James A. Fay, Massachusetts Institute of Technology; Dr. Bernard Fisher, CERL/England; Dr. Douglas Fox, USDA Forest Service; Dr. Robert Friedman, Office of Technology Assessment; Dr. Jerome Hales, Battelle PNL; Mr. Bruce Hicks, NOAA/ATDL; Dr. Daniel Jacob, California Institute of Technology; Dr. Oystein Hov, Norwegian Institute for Air Research/NILU; Dr. Frederick Lurman, Environmental Research & Technology, Inc.; Dr. Daniel McNaughton, TRC Environmental Consultants, Inc.; Dr. Gregory J. McRae, Carnegie-Mellon University; Dr. P.K. Misra, Ontario Ministry of Environment; Mr. Marvin Olson, Atmospheric Environment Service; Dr. Lars Prahm, Danish Meteorological Institute; Dr. Philip Roth, Consultant; Dr. Ian Rutherford, Atmospheric Environment Service; Dr. Perry Samson, University of Michigan; Mr. Frank Schiermeier, NOAA/MD ASRL; Dr. Jack D. Shannon, Argonne National Laboratories; Dr. George Slinn, Battelle PNL; Dr. Akula

Venkatram, Environmental Research & Technology, Inc.; Dr. Eva Voldner, Atmospheric Environment Service; Dr. Thomas Warner, Pennsylvania State University; Dr. Boris Weisman, MEP Company; and Dr. Fred White, American Meteorological Society.

The workshop had the following objectives: 1) To examine current understanding of the physical processes responsible for long range transport and deposition of atmospheric pollutants, with emphasis given to the uncertainty in our understanding of these processes; 2) To examine the parameterization of these processes in available long range transport models and to estimate the effects of parameterizations on model uncertainty; 3) To examine the temporal and spatial scales of applicability of the available long range transport models; 4) To examine the data base available for use in long range transport modeling and to the extent possible estimate the limits of predictability associated with the use of this data base; 5) To recommend methods to test long range transport model results with corresponding observations with a view to quantifying model uncertainty; and 6) To produce a report summarizing the workshop findings. A series of invited draft chapters were prepared and distributed to discussion leaders several weeks prior to the meeting. The draft chapters provided a focus for discussion at the meeting and were intended to raise the pertinent scientific issues to be addressed by the working groups and to aid in the preparation of findings and recommendations. The workshop report refinement process occurred via the plenary discussions and working group sessions held throughout the 3 1/2 days.

This AMS publication contains a complete documentation of the workshop including the revised chapters, and the full reports of the Eulerian and Lagrangian working groups. A summary document was published in the Bulletin of the American Meteorological Society Vol. 66, No. 12, 1533-1540, 1985.

CHAPTER I

A POLICY PERSPECTIVE ON LONG RANGE TRANSPORT MODELS

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United States Congress
Washington, DC 20510

The views expressed in this paper are entirely those of the author and are not necessarily those of OTA.

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INTRODUCTION

The purpose of this presentation is to bring a bit of the policymaker's perspective to this workshop. To meteorologists, atmospheric chemists and other experts involved in model creation, the model itself--the structure, the implementation, each parameter and so on--is extremely important. But policymakers are not interested in models per se. They want information. They want it from experts. And more often than not, they need the information before the expert feels comfortable drawing firm conclusions from it. I will discuss each aspect in turn.

Martin Greenberger pointed out that "Experts create models, but models also create experts... As a general rule, the modeler is far more important than the model in providing input to policy discussions" (Greenberger et al., 1976).

To support his assertion, Greenberger discusses a pollution transport model in a different medium--a water quality model of Jamaica Bay, New York developed by Jan Leendertse. Leendertse and his model were involved in at least five regionally important water quality decisions. According to Greenberger, "Although his model was often assumed to have directly affected numerous water resource policy decisions, in reality it was little used for direct decision-making. Much of the discernible impact on policy was due to Leendertse and only indirectly to his model, which was unable to answer fast-changing policy questions. But the model did help Leendertse expand his understanding of the Bay and develop his more adaptable mental model."

A model can certainly help you get to the witness table at a Congressional hearing, but once there, you are on your own. Almost invariably, policy-level questions require you to synthesize a vast amount of experience--that is, exercise a mental model rather than report on a single computer model run.

The difficult part of the art of modeling is knowing how to judge the limits of both the model's uses and the modeler's knowledge. Sometimes we overstep the model's bounds, placing too much confidence in its results. At other times, we err on the opposite side. We underestimate our depth of understanding simply because all aspects are not modeled. Throughout this workshop, the participants must be conscious of finding the mid-point between these two extremes.

In my own experience as a technical analyst I find it easy to drift to either side. This is especially true when, as often happens, information is needed before I feel comfortable drawing firm conclusions.

Model builders have another option when their nerve begins to fail. It is known as the "artichoke phenomenon". I mention it because it is a trap that this workshop could easily fall prey to.

According to Brian Crissey, the artichoke phenomenon is "the process by which models grow in response to criticism. Somebody says, oh, but you didn't include X and so you slap another horny plate on there. Eventually you have the artichoke which is all sharp and pointy on the outside and the really interesting things are down inside where you can't see them. The thing keeps on growing until finally there are so many points on the outside that no further critics wish to handle it, hence the criticism stops and the model is complete (Crissey, 1979).

At the risk of sounding like I'm preaching, I hope this workshop does not become an exercise in artichoke building. Policymakers need to know "the really interesting things" that are down inside where they can't now see them. Imagine how much more valuable the workshop proceedings will be if we strive to enlighten, rather than provide a list of possible horny plates.

I could continue to fill this paper with my own thoughts and biases about the use of models for environmental decision making, but you would then only have one person's views. After all, I am not a decision maker. Rather I am a technical assistant who--like a "good child"--responds only when spoken to.

I have been in a position, however, to observe Congress as it has handled the issue of acid rain for the past four years. I will recount a rather myopic history of acid rain control bills introduced into Congress over the last few years, discussing only those aspects germaine to LRT model use. One can then get a feel for how real policymakers--not conference surrogates--have dealt with LRT models. I hope that this will give insight into how they may be used in the future.

Following the brief history, I will discuss how LRT model uncertainty fits into the broad policy question of whether, or when, to control transported air pollutants.

AN HISTORICAL PERSPECTIVE

A. Acid Precipitation Act of 1980

The only law specifically concerned with acid deposition is the Acid Precipitation Act of 1980 (Title VII of the Energy Security Act of 1980, PL 96-294), signed June 30, 1980. Many, possibly most, of the attendees at this conference receive some research funds from the programs established by this law. The Act calls for an inter-agency effort that includes, among several others, programs for:

"research in atmospheric physics and chemistry to facilitate understanding of the processes by which atmospheric emissions are transformed into acid precipitation;" and

"development and application of atmospheric transport models to enable prediction of long range transport of substances causing acid precipitation."

The results of the research are to be used to "formulate and present periodic recommendations to the Congress and the appropriate agencies about actions to be taken by these bodies to alleviate acid precipitation and its effects."

B. The First Control Proposals

Many members of Congress did not feel that the Acid Precipitation Act of 1980 adequately addressed the concerns of their constituents. During October 1981, two bills were introduced to reduce sulfur dioxide emissions specifically to control acid deposition. The Mitchell bill and the Moynihan bill (S.1706 and 1709, respectively, of the 97th Congress) required about 35 percent to 45 percent reduction in Eastern U.S. SO_2 emissions. Both approaches allocated emissions reductions directly to States, based on source characteristics alone.

About the only consideration of a "source-receptor relationship" appears in the choice of control region. Emissions control was confined to the easternmost 31 States. One aspect of the problem, acidification of surface waters, seemed at the time to be spread throughout the East from North Carolina through New England. The chosen 31-State region encompassed this area plus a border of adjacent States, recognizing that pollution is transported across State lines.

One other factor, I believe, influenced the choice of control region. Several studies by EPA and DOE had already analyzed the costs of a series of emissions control scenarios in this 31-State region. Thus, though these bills' sponsors could not yet point to analyses of the effectiveness of these control proposals, they could at least discuss the potential costs.

This illustrates the role and power of models for influencing the course of public policy. The early model-based costs studies pointed the way to cost-effective approaches to emissions reductions. The sponsors of S.1706 and S.1709 chose rather different approaches to allocating regional emissions reductions, but both incorporate findings from the early studies. Discussions of the advantages and disadvantages of the two bills focused on: 1) the equity of the distribution of emissions reductions (a political judgement), and 2) the cost-effectiveness of emissions reductions (as analyzed by OTA and others using several available control-cost models).

Atmospheric transport models were not yet one of the tools in the policy analyst's tool box. Though known to Congressional staff, I believe they were viewed as a hindrance as much as an asset to the design of an emissions control proposal. To illustrate, a third bill was introduced during the same week as the Mitchell and Moynihan bills: S.1718 sponsored by Senator Dodd.

C. Modifications to the Existing Interstate Transport Provisions of the Clean Air Act

S.1718, rather than directly specifying emissions reductions, attempted to clarify and strengthen existing provisions of the Clean Air Act that regulate interstate transport of certain air pollutants. During the Act's 1977 reauthorization, provisions were added to prevent a State's emissions from causing violations of National Ambient Air Quality Standards in other States. Several States have attempted to use these provisions, either through petitions to EPA or litigation in Federal courts, to force other States to curb emissions. To date, few of these suits or petitions have been settled. One of the areas of contention is over how interstate effects are to be demonstrated.

In reviewing emissions limitations with respect to the interstate provisions, EPA only considers impacts that can be estimated by models approved under its modeling guidelines. This effectively limits consideration of impacts to within 50 km of the source, because there are no approved models to estimate long range transport impacts. Several States have objected to EPA's position and have attempted to compel EPA to use models and other techniques to assess long range pollution transport (OTA, 1984).

S.1718 specifically addresses this controversy over the use of LRT models. It would prohibit EPA from relying solely on models when considering interstate pollution and transport.

The bill received the support of the Senate Committee on Environment and Public Works and was combined with other provisions into a comprehensive Clean Air bill in both the 97th and 98th Congresses (S.3041 and S.768 respectively). The Committee report states (U.S. Senate, 1984):

> "In considering petitions under sections 110(a)(2)(E) or 126 the Administrator may not require the petitioner to rely solely on modeling or other methodologies previously approved by the Administrator for estimating interstate air pollution, but shall also consider--
>
> (1) the total loadings of any pollutant emitted from sources in the affected air quality control regions in each State subject to the petition;
>
> (2) reasonable estimates of the contribution to air quality problems in the petitioning State that come from sources outside the State;
>
> (3) the prevailing winds and other meteorological factors affecting the transport of any pollutant between the affected air quality control regions;
>
> (4) the comparative economic impact, including but not limited to, the impact on jobs and the potential for economic growth in affected air quality control regions in each State subject to the petition, of making such a finding or denying such petition, and;
>
> (5) such other factors as the Administrator may establish by regulation."

Thus, I believe the Committee was stating that though they felt LRT models could certainly provide some useful information about interstate pollution transport, lack of a definitive model was in no way to excuse the Administrator from issuing a decision. EPA was to issue a decision on interstate pollution complaints using all available information, even though such information was incomplete and its accuracy uncertain.

Some might argue that this illustrates the difficulty Congress has understanding the uncertain world of science. I would argue the contrary: technical analysts are typically less comfortable with uncertainty than politicians. (Perhaps this stems from putting both your job and ego on review every two to six years. Contrast this to university tenure or civil service job security).

D. A Request for Model Use

Though most of the discussion of the Mitchell and Moynihan acid rain control bills concentrated on State-level allocation of emissions reductions and costs, the Senate Environment Committee did make one formal request for LRT model analyses. During a hearing on the two bills, Senator Moynihan asked OTA to compare the deposition reductions that might be achieved from the two approaches (U.S. Senate, 1982).

Though many at this workshop might be shocked, I believe that the Senator's request was reasonable. The Committee had been presented with analyses of differences in costs and emissions reductions mandated by the bills. Eventually they would have to accept one or the other (or neither) of the two proposals, but not both. Could LRT models help Congress decide between the two bills? I think the correct answer was that the bills were so close that models could provide little insight--of itself a useful piece of information. I believe the reaction of the modeling community to the request dissuaded the Committee from asking the question again for several years. The request from the Committee was not totally naive. They understood that several LRT models were being evaluated by a joint U.S.-Canada technical work group under the Memorandum of Intent on Transboundary Air Pollution signed by the two countries. OTA was asked to coordinate analyses of the three U.S. and two Canadian LRT models then undergoing review. By having each of the modeling groups exercise their model for both bills and then discuss their results, the Committee hoped to obtain the opinion of technical community about the differences between the two bills.

What they (and OTA) misjudged was the intensity of feeling about the use of these preliminary diagnostic tools for policy purposes. Some of this was due to political pressure, both real and imagined; some was due to legitimate fears about potential misunderstanding and misuse of their results.

Only one of the five modelers responded formally to the OTA request. Others met with us secretly, handing over computer drawn maps as if they were stolen, top-secret national defense plans. Eventually OTA was able to informally discuss the results from most of the models with Committee Staff. I believe they found the briefing useful, but as one might expect, limited. It was a poor substitute for the workshop for models the Committee and OTA had originally envisioned.

The LRT modeling community missed an excellent opportunity to educate Congressional staff. The modelers could have discussed the basic understanding and assumptions that form the basis of any LRT model, and the subtle differences among the available tools. Of greatest importance, the modelers could have explained the types of information that models can provide and the types of questions that are beyond their resolution. (The difference between the Mitchell and Moynihan bills primarily fall into the latter category, except for the obvious difference that the Mitchell bill mandated 25 percent greater emissions reduction.)

In case any of you were wondering, OTA did publish one set of model results, those provided by Jack Shannon using the ASTRAP model (OTA, 1982). No flashes of lightning or peals of thunder resulted. The analysis provided another reasonably useful piece of information to decision makers weighing many policy considerations.

E. S.2001, 98th Congress

Though about a dozen emissions control proposals were introduced over the two years following the Mitchell, Moynihan, and Dodd bills, to my knowledge none made use of LRT models. The concept resurfaced in a bill introduced by Senator Durenburger in October 1983. More than one joke referred to the similarity between the bills number (a chance occurrence) and the title of a Stanley Kubrick movie. In 2001 (the movie) many decisions were made by HAL, the computer. S.2001 (the bill) requires the EPA Administrator to publish a "priority list" of emissions reductions, determined using several criteria. Two of these implicitly require the use of models.

The bill states that the priority list shall: 1) "assign highest priority to ... sources which will achieve the greatest degree of emissions reduction for each dollar" of public cost (as specified by a formula in the bill), and 2) "reflect scientific knowledge concerning the relationship of emission sources to receptor areas for areas or natural resources particularly sensitive to acid deposition."

Similar to most of the other control proposals, the bill specifies the total required emissions reductions (10 million tons of sulfur dioxide). But unlike other proposals, the bill requires that the allocation of emissions cutbacks to sources and States is to be determined by EPA following a series of technical analyses. (Perhaps with HAL's assistance?)

This is not the only controversial aspect of the bill. For example, S.2001 would also impose a tax on emissions of sulfur and nitrogen oxides. Both aspects may have contributed to the lack of cosponsors for the proposals.

There may, however, be a lesson here. The Durenburger proposal recognizes that there is a role for LRT models in acid rain control. The bill assigns LRT models and modelers to the role of advisors to the EPA Administrator. The Administrator is to weigh this information along with many other considerations and construct an overall priority list for emissions reductions. My guess is that though many might have supported the role of LRT models and modelers as advisors (not as decision makers), leaving the eventual decision of which sources were to reduce emissions to the EPA Administrator did not win many supporters. The technical objectives are certainly reasonable, but perhaps the advisory role should occur at a different stage in the process.

F. Reaction on the House Side

During all of this Senate activity, the House of Representatives, of course, was not idle. Several acid rain control bills had been introduced, but similar to most of the Senate proposals, emissions reductions were based on sulfur dioxide emission rates rather than knowledge of detailed source-receptor relationships.

I was present at an interesting discussion about the availability of a new model. The tool was a linear-programming model that incorporated both a simplified control cost model and a source-receptor matrix. Several groups were present at the discussion, represented by technically oriented staff rather than policy types. Someone got the bright idea that using such a model to generate a "least-cost control program" might attract a good deal of interest.

What was being proposed, of course, was an exercise similar to S.2001. Rather than have the EPA Administrator issue a priority list, however, the model could be used to solve the "optimal" State-level allocation of emissions reductions. This State-level list would form the basis of a bill. A few "minor" problems: What were the goals? To reach a specified deposition level in all areas? Some areas? What deposition level? And so on.

What was needed was a "policymaker," in particular, a member of Congress who would express interest in such an approach and specify the goals. OTA was invited to the meeting because we were the technical support group most likely to be asked to exercise the model. I was a bit skeptical that an interested member of Congress would be found, but was certainly willing to attempt the analysis if a relevant Committee requested it.

I was fortunate to be present when a member of this group proposed using this model to the staff of one of the appropriate Committees. Without hesitation, the staffer replied "You're not going to drag that dead horse in here." Discussion closed.

I assume he felt that such an exercise would be futile; he had no desire to waste his time and the time of the members of his Committee "beating a dead horse." One might have thought that such a model would be more of a young colt than a dead horse. My guess as to why the staffer might feel this way is that he had been present through much testimony describing the need for a "perfect" LRT model. With the atmospheric science community this divided, there was little political advantage in pursuing this approach.

CHARACTERISTICS OF THE POLICY PROBLEM

Though four years have passed since the introduction of the first acid rain control bill, the highly controversial public policy issue of whether or not to take action to further control pollutant emissions still remains. Several characteristics of transported air pollutants have fueled the public policy debate. First, scientific uncertainty exists over the extent of the consequences of transported air pollutants, and the effectiveness of pollution control. Second, significant disagreements in values exist over how to balance the costs of controlling pollutants and the environmental risks posed by pollution. Third, and of great political importance, transported air pollutants pose a distributional problem, having intersectoral, interregional, international, and intergenerational equity aspects.

A. Disagreements Over Facts

Debate over scientific understanding of transported air pollutants is perhaps the most visible aspect of the policy controversy. Many assert that the causes and consequences of acid deposition are both sufficiently understood and significant to warrant immediate action to control it. Others emphasize the complexity of the phenomena involved, and argue that until more is known about the benefits of control, no regulatory strategy can be justified on the basis of existing scientific knowledge.

One must keep in mind, however, that scientific uncertainty is not new to air pollution policy. The continuing controversy over the nature and magnitude of health risks--the critical measure for setting national ambient air quality standards--is perhaps the most obvious example of the difficulty of unambiguously documenting the scientific basis for regulation.

B. Disagreements Over Values

Disagreements over facts about transported air pollutants are accompanied by disagreements over values. Even if a scientific consensus existed on the magnitude of the problem of transported pollutants, policy choices would still be complicated by lack of agreement over how to promote economic development while protecting the environment. Although the concept of a trade-off between these two values is widely accepted, various individuals and groups differ sharply on where the balance should be struck.

Disagreements over facts and values are intertwined. Differing value structures among various individuals and groups lead each to draw quite different conclusions from the same body of scientific information. Widespread recognition of scientific uncertainties has focused the policy debate on whether or not both the magnitude of damage involved and the effectiveness of control efforts are sufficiently known to pursue emissions reductions. This dispute involves both relatively objective issues of science, e.g., how reducing sulfur emissions might affect sulfur deposition in certain areas, and subjective issues of values, e.g., what level of scientific certainty and/or what degree of damage is required to justify undertaking a control program.

I urge all the workshop participants to keep this distinction clearly in mind. One of the major challenges of the next few days will be to characterize LRT model uncertainty in such a way that policymakers can use this information, along with their values, to make these decisions. Though it is extremely difficulty to keep our own values from coloring our technical opinions, we must constantly monitor ourselves to ensure that this does not happen.

C. Distributional Issues

Additional value conflicts arise from the distributional aspects of transported air pollutants, further complicating the policy dilemma. Pollution control, by internalizing environmental costs, affects the relative prices of various products, and thus the allocation of economic resources among sectors. Economic activities that are inherently less polluting, or that can reduce pollution less expensively, may gain at the expense of more pollution-intensive goods and services. But the geographical scope of transported air pollutants creates several distributional issues not present in conventional, local air pollutant problems.

Winds carry pollutants over long distances, so that activities in one region of the nation may contribute to resource damage in other regions. Many of these activities primarily benefit the source region, while some of their costs, in terms of resource damage caused by the eventual disposal of their waste products, are incurred by other regions. Long range pollution transport thus redistributes benefits and costs among regions. Programs to control transported air pollutants would also have inter-regional distribution aspects. The costs of controlling emissions might be imposed primarily on the source region (depending on the scheme for allocating costs), while the major benefits of reducing emissions might accrue primarily to the downwind, receptor region.

It is because of the distributional aspects that LRT models can offer much to the policy debate. At the same time, however, we must recognize that many types of distributional issues--not merely source-receptor relationships--must be considered.

If transported air pollutants are believed to cause sufficient damage to warrant reducing pollutant emissions, designing control policies will be difficult both analytically and politically: analytically, because of the problem of identifying the sources that can most efficiently reduce the risk of resource damage in sensitive areas; politically, because placing the burden of control on certain regions may appear to be arbitrary or inequitable.

KEY SCIENTIFIC UNCERTAINTIES

Though the focus of this workshop is uncertainty in LRT models, to policymakers, this is only one of several important technical considerations. I find it difficult to place LRT model uncertainty into perspective without considering how it fits with other scientific questions.

Five key uncertainties are especially relevant to policy-level decisions about transported air pollutants. These include controversies about 1) the extent and location of current damages, 2) future damages (whether they are cumulative and/or irreversible), 3) the geographic origins of observed levels of pollution, 4) the effectiveness of emissions reductions for reducing observed levels of transported pollutants, and 5) whether a research program will provide significant new results.

These scientific uncertainties affect several policy concerns, including: 1) making air pollution control policy as fair as possible, i.e., providing some legal recourse to those bearing the risks of damage, and (if a control program is adopted) distributing costs of control fairly; 2) the inter-generational implications of the risks of cumulative and irreversible damage; 3) weighing the risk of damage against gains that might be achieved by waiting for better information or improved technology; 4) assuring that the benefits, in the broadest sense, of a control program justify the cost.

I feel it is important that as a group we recognize each of these uncertainties, not just those that relate to atmospheric science. Let me briefly discuss why.

A. Uncertainty About the Extent and Location of Current Damages

Effects researchers are certain that transported air pollutants have caused some damages. At issue is the extent of the damage, whether it is fairly localized or widespread, and which resources are affected. For example, there is little question that acid deposition damages lakes, and ozone harms crops. For other concerns, for example, damage to forests from acid deposition and ozone, the uncertainties are so large that it is difficult to describe even the patterns or magnitude of the risk.

This situation makes the LRT modeler's job quite difficult. Ecologists cannot provide LRT modelers with neat and tidy "dose-response functions" for the modeler to use when contemplating alternative model structures.

The "range of useful" spatial and temporal resolution of pollutant air concentration or deposition varies by resource. I use the phrase "range of useful" resolution to emphasize that no single dose response formulation is agreed to by effects researchers.

For example, ozone exposure to crops is expressed many ways: growing season average daytime concentrations, seasonal average peak hourly concentrations, percentage of time above a threshold, etc. Target deposition values to protect sensitive aquatic resources have also been estimated many ways: annual wet sulfur deposition, annual total sulfur deposition, weighted annual hydrogen ion concentration in precipitation, etc.

In general, seasonal to annual averages are appropriate for most living systems. Given limitations in data and understanding, many alternative exposure statistics are possible. The choice of statistic for the eventual goal of estimating resource damage is by necessity a compromise between atmospheric scientists and effects researchers.

As I look down the list of attendees I am disappointed to see that few "land and water" (as opposed to air) scientists are in attendance. It will be difficult to meaningfully discuss such topics as the appropriate temporal and spatial scales of LRT models without a full complement of effects researchers (e.g., aquatic biologists and chemists, foresters, and material scientists). Though it is too late to add the advice from other disciplines to this workshop, each of you should invite an ecologist or other effects scientist to lunch within two months. Both the free lunch and the chance to discuss his or her information needs would be appreciated.

B. Uncertainty About Future Damages

For some resources, pollution-related damages might worsen over time if pollution remains at about current levels. The extent to which damages accumulate--and over what time scale--has played a major role in the policy debate over the risks of delaying control action. If damages are not significantly cumulative, delaying control action while awaiting further information would not increase the level of damage from year to year (assuming that the level of pollution remains fairly constant). However, for those effects of transported pollutants that are cumulative, the longer control actions are delayed, the greater the severity of the damage.

A closely coupled concern is whether damage can be easily reversed, and if so, over what time period? For example, the effects of a severe series of ozone episodes, or the potential cumulative effects of acid deposition, will persist in the forest community until a new forest grows.

Uncertainties about the irreversibility of resource damage make delaying control action until better information is obtained highly controversial. To the extent that damages are both significantly cumulative and irreversible, waiting for better information would cause resources to be irretrievably lost for this generation and the next several to follow.

I will repeat a saying that I have often heard in Washington--one that usually sounds strange to scientists. There is a difference between being "right" and making the "right decision." The former refers to an absolute; the latter recognizes that delaying an action is as much a decision as is proceeding.

Policymakers strive to make the "right decision." Hindsight may show that another course of action was "right," but all one can truly hope for is that the policymaker acted in a manner consistent with the best information available at the time. Knowing that there are risks from waiting, a major challenge for the workshop participants will be to communicate a sense of the best information available at this time, and an appraisal of what might be known in the near future.

C. Uncertainty About the Origin of Observed Levels of Transported Pollutants

1. Pollutants leading to acid deposition

If one wishes to reduce current levels of pollutants, the next logical question is, "Where are they coming from?" Three questions are important: 1) whether the precursor pollutants are of natural or man-made origin; 2) whether they come from local sources (and therefore well suited to the existing structure of the Clean Air Act) or from distances exceeding hundreds of kilometers; and 3) whether it is possible to define the geographic origin of pollutants deposited in a particular region.

One of the major concerns of this workshop is whether we can now--or in the near future--reliably determine how much of the deposition in any one region originates from emissions in any other. To my knowledge, about a dozen computer models of varying sophistication are now available to perform such analyses, but their accuracy in portraying this relationship is uncertain. Describing this uncertainty is important for several policy reasons.

Model adequacy is a critical element in several suits and petitions by States to control transported air pollutants under the interstate provisions of the current Clean Air Act. EPA considers available models to be inadequate to address the question of long range pollution transport; consequently, the agency does not assess the effects of pollution that travels beyond 50 km. However, the petitioning States assert that available "long range transport" models reflect the state of the art and should therefore be used by EPA. Both arguments have some merit; I hope the question of model uncertainty is discussed at this workshop from both viewpoints.

In addition, policy-level attempts to focus reductions in pollutant deposition on identified, sensitive regions would rely to a large extent on model-based abilities to determine the sources of such deposition. However, no amount of accurate, detailed modeling information would be sufficient to eliminate policy disputes over which region's resources should be protected, or which region's emissions should be controlled. Because many regions have sensitive resources, and all of them receive some deposition from each of many emitting regions, a variety of possible strategies could be used to reduce deposition on sensitive resources.

For example, policymakers, in response to equity considerations, could develop control programs under which regions responsible for "large" shares of deposition in "several" sensitive regions bear the "greatest share" of emissions reductions. Whether the broad regional patterns of transport described by existing LRT models are accurate enough for this purpose is as much a policy question as a scientific one. The atmospheric scientist's part of the bargain is to describe the confidence he or she has in the results at various spatial and temporal scales. There is no single spatial and temporal scale that is inherently superior; each has its own political advantages and disadvantages.

The de facto standard resolution for emissions is State-size areas over annual time periods. Given the momentum of the emissions control bills proposed over the last several years, compelling scientific reasons would be needed to alter this standard. This group should address, for instance, whether we are yet able to discern the effects of within-State variations in emissions patterns (not totals) on deposition several hundred kilometers away. And if so, how large are the differences so that policymakers can compare them to the advantages of allocating emissions reductions to States rather than sources.

The group should also focus on seasonal to annual time scales--single years, if necessary, but multi-year averages, if possible. Shorter time-scale models might be necessary for diagnostic purposes, but I have difficulty envisioning a shorter time-scale regulatory program.

2. Pollutants leading to ozone formation

The same questions apply to ozone: whether the precursor pollutants are of natural or man-made origin, whether they are of local or distant origin, and--more generally--whether it is possible to identify the geographic sources of elevated ozone concentrations in a specified region. As with acid deposition, ozone levels over broad regions of the United States exceed natural background levels. Though locally produced ozone is a problem in many of the nation's urban areas, the chemical precursors are thought to travel long distances, and elevated ozone levels are found in rural areas downwind from sources of these precursors.

It is my understanding that models of long-range ozone transport are in a rather rudimentary stage of development. I strongly urge that this workshop spend some time discussing long range ozone (and precursor pollutant) transport. A description of the current status and future prognosis for ozone models would be extremely useful from a policy perspective, especially if compared to sulfur transport models. Of particular interest are models that can characterize growing-season ozone concentrations over areas the size of the Eastern United States.

Recent documentation of tree productivity declines throughout widespread areas of the Eastern U.S. has accelerated the need for such tools. I am certain that ozone transport will be discussed much more widely during the next Congress than it was during the past few years' Clean Air Act reauthorization debates.

D. Uncertainty About the Effectiveness of Emissions Reductions for Reducing Observed Levels of Transported Pollutants

Much of this workshop will be devoted to discussing the numerous complex chemical transformations that occur as pollutants are transported. Special attention will be paid to the uncertainties that exist about how effective reducing emissions of each precursor pollutant will be in controlling the transformed products.

For example, several analyses indicate that cutting back regional sulfur dioxide emissions alone will significantly, but not quite equally, reduce the amount of sulfur deposited in various forms. Because other pollutants (such as hydrocarbons and nitrogen oxides) can enhance or impede chemical transformations of sulfur dioxide, simultaneous control of other pollutants might also be used to reduce sulfur deposition.

Uncertainties about which pollutants to control, as well as the uncertain relationship between emissions reductions and deposition reductions, complicate the policy objective of reaping the greatest possible benefit from the costs of controlling emissions. Using current LRT models, scientists are unable to confidently project the precise pattern of deposition reductions that will result from a specified emissions control plan. Under these circumstances, a control program designed and implemented today might not produce the maximum benefits achievable for a given cost. But how far wrong might current models be? Stated another way, how much more efficient or cost-effective will an emissions control program designed five years from now be? Much of the workshop will be devoted to discussing these uncertainties and making recommendations for improvements in LRT models. I urge the group to include a clear statement of need and possible gains along with each modeling recommendation.

E. Uncertainty About Whether a Research Program Will Provide Significant New Information

One of the most difficult decisions facing the Congress is whether to act during this reauthorization of the Clean Air Act, or to wait for results from ongoing, multi-million dollar federal and private research efforts on acid deposition. While the research efforts are intended to reduce the uncertainty discussed above, how much new insight 5 to 10 years of further research will provide is unknown.

For example, years to decades are required to observe changes in many ecological processes. Patterns of crop yield and forest productivity typically vary from year to year; separating the effect of acid deposition and ozone from normally expected year-to-year fluctuations requires many years of data.

Uncertainties about the progress of research programs are an important factor when considering the timetable for policy decisions. Given the planning, contracts, construction, and so on necessary to significantly reduce pollutant emissions, a decision to control emissions now may still require 10 or more years to implement. Waiting five to 10 years for the results of a research program before deciding to control emissions increases the time required to reduce deposition from 10 years to 15 or 20. Delaying control action increases the risk of resource damage but reduces the risk of inefficient control expenditures.

Such delays could be avoided by mandating controls now, while retaining the option to change the law if new research results show an alternative action to be preferable. To achieve compliance within a decade, however, expenditures would have to begin within five to seven years. If results suggesting an alternative control strategy appear much after this time, major expenditures may be irrevocable.

While much is known about the basic mechanisms of acid formation and deposition, detailed knowledge of the complex chemistry and meteorology involved will require many more years of research. Efforts to evaluate the current generation of computer models that simulate atmospheric processes have already taken several years.

The number of years needed to significantly improve existing models is an extremely useful piece of information for policymakers. Estimates of the timing of expected improvements should accompany each of the workshop recommendations. The five year horizon discussed above is a convenient and useful reference point.

REFERENCES

Crissey, B., 1979. Models in the Policy Process: A Framework. **In**: Utility and Use of Large Scale Mathematical Models, S.I. Gass (Ed.), National Bureau of Standards Special Publication 534.

Testimony by Robert Friedman, 1982. **In**: Senate Committee on Environment and Public Works. Acid Rain: Hearing on S.1706, S.1709, and S.1718. Serial No. 97-H30, U.S. Senate.

M. Greenberger et al, 1976. Models in the Policy Process. Russell Sage Foundation, NY.

Office of Technology Assessment, 1982. **Regional Implications of Transported Air Pollutants**. Interim Draft, July. Section L.

For a review of this issue see: Office of Technology Assessment, **Acid Rain and Transported Air Pollutants**. OTA-0-204, 1984. Appendix D.

Senate Committee on Environment and Public Works, 1984. **Report to Accompany S.768, 98th Congress**. Report 98-426, U.S. Senate, 1984.

CHAPTER II

SOURCES OF ERROR AND UNCERTAINTY IN EULERIAN LONG RANGE TRANSPORT MODELS

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INTRODUCTION

The regional-scale phenomena of photochemical oxidants, acidifying compounds, and their precursors are complex and coupled. Analyzing the causes and effects of changes in their cycles and determining source-receptor relations is critical since the presence of pollutants can greatly influence health, weather, climate and agriculture.

Modeling plays an essential role in understanding long range pollutant transport. It provides a way to close the loop between field experiments and understanding the chemical and physical phenomena of pollutants in the troposphere. Field measurement programs, even with extensive spatial coverage, identify a subset of the troposphere only for limited periods of time; and laboratory studies elucidate only a limited number of processes under idealized conditions. Verified models can be used to project the air quality at different times and under different conditions. However, models characterize the complex atmospheric processes (which are incompletely understood) by use of chemical, dynamic and thermodynamic parameterizations. They also require the specification of meteorological inputs, and initial and boundary concentration fields. Thus, there are many sources of errors and uncertainties that can influence the model performance. The utility and improvement of long range transport model requires the assessment of these errors. The major errors and uncertainties in Eulerian long range transport models are discussed in this chapter.

SOURCES OF ERROR AND UNCERTAINTY IN THE MODEL FORMULATION

A. Overview

The goal of developing long range transport models is to be able to specify the concentrations of pollutants given information on the meteorology, the source distribution, and the initial conditions. Two distinct alternative kinds of specification are possible. The Eulerian type defines concentrations as functions of position in space and time. This specification provides a picture of the spatial distribution of material at each instant during the motion.

The Langrangian type of specification describes the dynamical history of selected material elements. This approach is more fundamental in that it recognizes that some of the dynamical or physical quantities affecting pollutant transport refer not only to certain positions in space but also to identifiable pieces of material. The Langrangian type of specification is useful in pollutant modeling (see Chapter III) but is difficult to apply to non-linear chemical reaction flow situations. It is also at a disadvantage in that it does not supply directly the spatial gradients in the pollutant fields.

The Eulerian modeling approach is the subject of this discussion.

1. Basic equations

The mathematical basis for Eulerian modeling of pollutant transport is the species continuity equation.

$$\begin{aligned}\frac{\partial C_i}{\partial t} + \frac{\partial}{\partial x_\alpha} (\tilde{u}_\alpha C_i) = {} & \frac{\partial}{\partial x_\alpha} D_i \frac{\partial C_i}{\partial x_\alpha} \\ & + R_i(C_i, \ldots, C_N, T, h\nu, L) \qquad (1) \\ & + S_i(x_\alpha, t)\end{aligned}$$

where C_i is the concentration of species i, $\tilde{u}_\alpha$ is the α component of the elocity field, D_i is the molecular diffusivity of species i, R_i is the rate of formulation of species i, T is the temperature, $h\nu$ is the photon flux, L is the water concentration, and S_i is the source term.

Equation (1) describes the instantaneous concentration values. The use of this equation requires precise information of the temporal and spatial nature of the velocity field, $\tilde{u}_\alpha$. However, the turbulent motions in the atmosphere used in air pollution models are either determined from observations or from the solution of a fluid dynamic simulation model. In either case the velocities are known only at discrete points in space and time. Lamb and Seinfeld (1973) have shown that only features of the velocity field with spatial scales larger than twice the average distance between sampling points can be described explicitly.

The conventional way of dealing with incomplete knowledge of the turbulent velocity field is to represent the velocity as a sum of the deterministic velocity u_α and a random component u_α' (i.e., $\tilde{u}_\alpha = U_\alpha + u_\alpha'$). Because u_α' is a random variable, Eq. (1) represents a stoichastic differential equation and C_i itself is a random variable. The probability density function describing C_i cannot be determined in general. However, the expected value of the species concentrations, $<C_i>$, are governed by

$$\frac{\partial <C_i>}{\partial t} + \frac{\partial}{\partial x_\alpha} (U_\alpha <C_i>) + \frac{\partial}{\partial x_\alpha} <U'_\alpha C_i'>$$

$$= D_i \frac{\partial^2 <C_i>}{\partial x_\alpha \partial x_\alpha} + <R_i> + S_i(x_\alpha, t), \tag{2}$$

Equation (2) is the basic equation for the ensemble mean concentration of a reactive pollutant in the atmosphere and is the underlying equation for Eulerian models. However, the direct solution of (2) is precluded by the appearance of the new dependent variables, $<u_\alpha' C_i'>$ and any similar variables arising from $<R_i>$ (e.g., $<c_i' c_j'>$).

In most applications it is assumed that

$$<u'_\alpha c_i'> = K_{\alpha x} \frac{\partial <C_i>}{\partial x_\alpha}, \tag{3}$$

that the ensemble mean reaction rate can be represented by the reaction rate based on the mean concentrations, and that molecular diffusion can be ignored relative to turbulent mixing. Under these assumptions Eq. (2) becomes

$$\begin{aligned}&\frac{\partial\langle C_i\rangle}{\partial t} + \frac{\partial}{\partial x_\alpha}\left(K_{\alpha\alpha}\,\frac{\partial\langle C_i\rangle}{\partial x_\alpha}\right)\\ &+ R_i(\langle C_i\rangle, \ldots, \langle C_\nu\rangle, \ldots) + S_i(x_\alpha, t)\\ &- G_i(\langle C_i\rangle, \ldots, \langle C_\nu\rangle, \ldots)\end{aligned} \tag{4}$$

where the term G_i is added to represent the mass transfer for gas phase-to-dispersed phase interactions (e.g., gas absorption). Higher-order closure models are being developed to deal with the fluctuation terms (Lewellen and Teske, 1975; Donaldson et al., 1972). These terms will be discussed in more detail in later sections.

Equation (4) is the standard form used in Eulerian modeling of pollutant transport. It represents an approximation of the mean concentration of reactive pollutants in turbulent flows. The predictability of (4) depends upon the flow, the source distributions, and the chemical reaction mechanism, and has been analyzed in detail by Lamb and Seinfeld (1973) and Reynolds et al. (1973). They conclude that Eq. (4) is valid under conditions where the reaction processes are slow compared to the turbulent transport and the characteristic length and space scales for changes in the mean concentration field are large compared with the corresponding scales for turbulent transport. These conditions imply that (4) is capable of resolving those features in the concentration field which have horizontal scales greater than 2 km, vertical scales greater than 20 m and temporal scales greater than 1000 s. Equation (4) may be invalid near strong isolated sources.

2. Model framework

The atmospheric diffusion equation (Eq. (4)) provides the mathematical framework for linking the various transport/chemical/removal processes in an Eulerian model. The basic processes and their component parts are shown schematically in Figure 1. The major components consist of: 1) a meteorological component (or module) to describe the wind speed and direction, the eddy diffusivity and mixing layer height, the temperature, the water

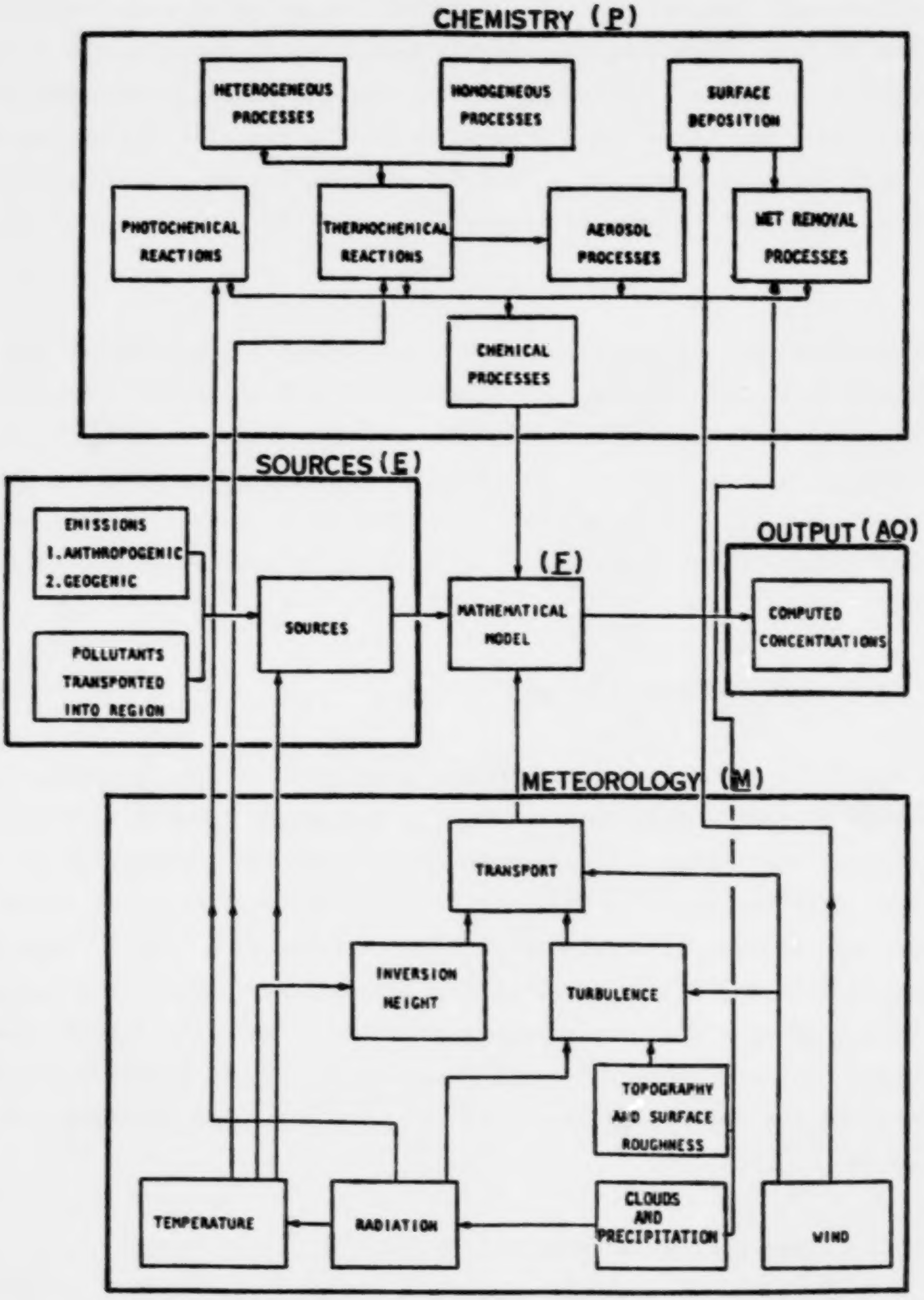
CHEMISTRY (P)
HETEROGENEOUS PROCESSES
HOMOGENEOUS PROCESSES
SURFACE DEPOSITION
PHOTOCHEMICAL REACTIONS
THERMOCHEMICAL REACTIONS
AEROSOL PROCESSES
WET REMOVAL PROCESSES
CHEMICAL PROCESSES
SOURCES (E)
EMISSIONS
1. ANTHROPOGENIC
2. GEOGENIC
POLLUTANTS TRANSPORTED INTO REGION
SOURCES
(F)
MATHEMATICAL MODEL
OUTPUT (AQ)
COMPUTED CONCENTRATIONS
METEOROLOGY (M)
TRANSPORT
INVERSION HEIGHT
TURBULENCE
TOPOGRAPHY AND SURFACE ROUGHNESS
TEMPERATURE
RADIATION
CLOUDS AND PRECIPITATION
WIND

Figure 1. Elements of Eulerian long range transport models (from McRae et al. (1982)).

vapor, cloud water content, and the radiation intensity of each location as a function of time; 2) a chemical kinetic mechanism to describe the rates of atmospheric reactions, including homogeneous gas-phase, heterogeneous, and liquid phase reactions; 3) a removal module to describe the dry deposition of material, and the in-cloud and below-cloud removal processes; and 4) a source component to provide temporal and spatial information of emissions.

Each process incorporated into a model is itself a very complex and incompletely understood phenomenon. Therefore, in formulating a long range transport model it is necessary to incorporate the processes into the model framework by utilizing chemical, dynamic, and thermodynamic parameterizations. The commonly used parameterization techniques as well as the major errors and uncertainties associated with them are discussed in the following section.

B. Processes/Parameterizations

The distribution of pollutants in the atmosphere is determined by the distribution of source emissions and by the transport, removal, and reaction processes that occur. For example, pollutants are transported by the mean winds, both horizontally and vertically, mixed vertically by turbulent diffusion, are removed by interactions with surfaces (e.g., soil, vegetation, particulate and dispersed water droplet surfaces, etc.), and transformed by homogeneous and heterogeneous reactions. Eulerian models incorporate these processes into the model framework by use of parameterizations which describe the underlying chemistry and physics. These processes are discussed in this section.

1. Transport/meteorological

The transport processes (referred to here as the dynamic meteorological processes) are incorporated into the model framework through the mean velocities, the eddy diffusivities, clouds, and the temperature and radiation effects on the reaction rate. The basic components of the treatment of the transport processes in Eulerian models is shown in Figure 1. Figure 1 also illustrates the coupling between the transport and the chemical and removal processes. It is generally assumed that the pollutant transport model can be decoupled from the meteorological equations. This implies that the presence of pollutants in the atmosphere does not affect the meteorology (thus most of the interaction arrows point outward from the transport component). However, particulates and gaseous pollutants can influence the meteorology by affecting the radiation budgets, by providing condensation nuclei for cloud formation, and by supplying additional heat through chemical reaction. McRae et al. (1982) have surveyed the current literature regarding pollutant feedback to the meteorology and conclude that regional scale climatology may be significantly affected by the presence of pollutants and that more experimental data is necessary to quantify the feedback mechanisms.

The convection/mixing processes affecting the long range transport of pollutants in the environment are three-dimensional and time-dependent. The spatial and temporal resolution of Eulerian models necessary to resolve the most important features in the observed concentration fields is still uncertain. However, recent field data are providing important insights into the regional structure of pollutant distributions. Data from the SURE intensive regional field study in 1978 indicate that the horizontal length scale of variability (the length scale over which the mean concentration in a given vertical layer varies by ± 50%) of primary pollutants (i.e., SO_2, NO_x) is less than 50 km, whereas that for secondary pollutants (i.e., sulfate O_3) is greater than 50 km (Blumenthal et al., 1984).

The SURE data set also shows the vertical extent to which pollutants are transported and mixed. Well mixed layers of a few hundred meters were observed in the night time and early morning periods and within the lower 1000-1500 m during midday. However, primary pollutants were usually well-mixed only at horizontal distances greater than 50 km from sources. Secondary aerosols were seen at elevated concentrations up to about 2500 m. High concentrations were also detected above the mixed layer in the early morning. Elevated layers of polluted air have also been detected by the airborne lidar measurements of Shipley et al. (1984). These measurements indicate that the local interactions of mixed layer and cloud processes can transport pollutants to elevated layers and produce inhomogenities in the vertical profiles of pollutants with scales as small as 200 m. These layers of polluted air can transport material over long distances and can go undetected by surface measurements.

These data suggest that the most important transport processes are convective transport, mixing layer dynamics, and cloud venting. The data also indicate that the calculation of 24-hour averaged concentrations may require horizontal grid spacings smaller than 50 km, and vertical spacings as small as 200 m with a vertical domain larger than the highest cloud venting height (i.e., 4-8 km). This resolution is much finer than current models.

a. Wind fields

The wind fields necessary to solve Eq. (4) on the temporal and spatial scales of the model must be obtained either from objective analysis of observed winds or by use of dynamic meteorological models. Both techniques suffer from the fact that measurements (for interpolation or initialization) are available only at a few locations, generally at ground level, and at discrete times. The resulting derived wind fields introduce error and uncertainty in the variation of the horizontal winds and in the determination and variation in the vertical winds. Evaluations of these errors have been performed by Kitada et al. (1984), Dickerson (1978), Goodin et al. (1979), Shieh (1984) and others. These results demonstrate that the derived wind field is quite sensitive to the methodology used in the analysis.

Mueller (1984) has analyzed the errors in the estimation of wind fields for long range transport models by comparing observed horizontal winds with those calculated by spatial and temporal interpolation of National Weather Service (NWS) rawin data collected at 0000 and 1200 GMT and those using the NWS Boundary Layer Model (BLM).

He found the following:

a. Wind direction estimates based on rawin data contained positive (clockwise) biases of from 13 to 25 degrees, depending on season, level and interpolation scheme. Directional biases in the BLM wind fields were considerably smaller, ranging from -2 to 10 degrees. Results from a previous study by Reisinger and Mueller (1983) support the finding concerning the positive wind directional bias using rawin data.

b. Biases were found in wind speed estimates at 109 and 1412 m AGL. The rawin data tended to underestimate the wind speed, whereas the BLM output tended to overestimate it. The rawin underestimates were as large as 1.6 m/s and the BLM overestimates were as large as 0.9 m/s. The magnitude of the biases were lower at 1412 m than 109 m.

c. Computed error standard deviations were from 10 to 20 percent of the absolute range of the speed error (0-20 m/s). Furthermore, the root-mean-square vector errors indicate that the location error in a model after one-hour time step would be between 12 and 25 km.

d. Intercomparisons of the computed error parameters indicated that the use of 12-hour constant meteorological wind fields, based on 0000 and 1200 GMT rawin data, produces errors much larger than those resulting from the use of linear temporal data interpolation.

e. BLM and rawin data fields were judged to be nearly equal in all error categories except bias. The BLM was slightly better in speed bias and clearly speed bias and clearly superior in their ability to minimize directional bias.

f. Both BLM and rawin data sets produced lower standard deviations for wind speed errors in summer than winter, and larger direction error in summer than winter. The vector errors showed no major seasonal differences at 109 m, but were 25 to 30 percent less at 1412 m in summer versus winter.

In addition to these errors, a potentially large uncertainty underlies the preparation of flow fields for long range Eulerian models. This uncertainty is associated with the fact that there is no unique derived flow field. Rather there is an infinite number of flows that satisfy the observational data (even if we have perfect measurements). By adding additional constraints to the problem (e.g., physical principals, historical or climatological data, etc.) the likelihood of occurance of a specific flow can be bounded more confidently. This problem is currently being quantified by R. Lamb.

An additional problem associated with derived wind fields is that they generally do not have zero divergence. Objective methods which use the continuity equation as a constraint and dynamic models that use the continuity equation in the formulation can have divergences greater than $10^{-6}s^{-1}$. Large divergences are expected in regions where large divergent or convergent horizontal flows occur, e.g., when steep changes of topography occur in the vicinity of sea breeze fronts, etc. The use of a non-zero divergent wind field in Eq. (4) results in the introduction of fictitious production and consumption terms. This effect is illustrated in Figure 2 where the divergence flow field derived from a dynamic sea/land breeze model and the calculated transport of an inert species are presented. Initially the pollutant was assumed to be uniformly distributed within the region at a concentration of 0.1 ppb. The correct solution for these conditions is also a uniform distribution with value 0.1 ppb. As shown, deviations as large as -40% - +20% are calculated with deviations correlating with the non-zero divergences.

The effects of non-zero divergences can also be important for the calculation of species involved in rather slow atmospheric reactions, (e.g., gas phase oxidation of SO_2). Table 1 shows the ratio of the calculated

TABLE 1

The effect of wind field divergence on the ratio of the effective reaction rate constant to the chemical reaction rate constant of typical atmospheric reactions.

$\nabla\cdot\vec{V}$§	$NO + O_3$*	$C_3H_6 + OH$**	SO_2 conversion***
10^{-6}	1.00	1.04	1.52
10^{-5}	1.00	1.40	6.15
10^{-4}	1.01	5.05	43
-10^{-5}	0.999	0.62	-4.15

§ unit; sec^{-1}

* treated as a pseudo-first order reaction with the rate constant 0.0163 sec^{-1} by assuming (O_3) is constant at 10^{12} molecules/cm^3 (≅40 ppb at the sea level)

** treated as a pseudo-first order reaction with the rate constant 2.6×10^{-5} sec^{-1} by assuming (OH) is about 10^{6} molecules/cm^3.

*** using the average of the observed values, i.e., 1.94×10^{-6} sec^{-1} (≅0.7 $\%hr^{-1}$), Hobbs et al.(1979)

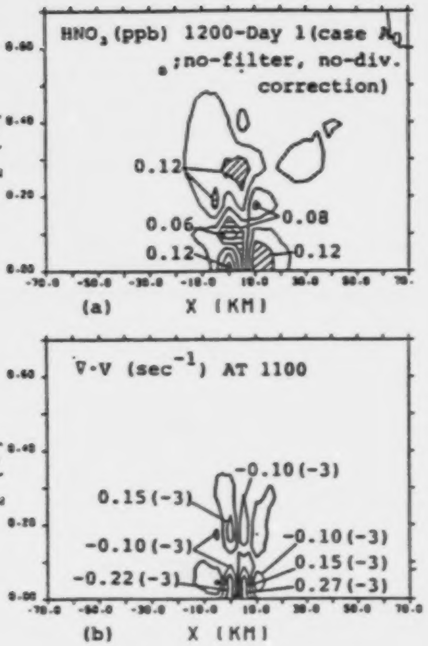

Figure 2. Calculated HNO_3 profiles (a) at 12:00 - Day 1 calculated using a sea/land breeze flow field with the divergence field in (b).

effective reaction rate constants to the true kinetic constant for various reactions as a function of divergence.

b. Eddy diffusivity profiles

The fact that the diffusion processes occur at different rates depending on time of day and location (both horizontal and vertical) plays an important role in determining the pollutant distribution in the atmosphere. The diurnal variations in the mixing layer provides a mechanism to transport material vertically in the atmosphere; and also a decoupling which allows, through the attendant nocturnal jets, the transport of materials over large horizontal distances above the surface nocturnal inversion before being brought to the surface the following morning as the mixing layer grows.

c. Cloud venting

Observational evidence (Isaac et al., 1984, Daum et al., 1983) suggests that clouds play an important role in distributing pollutants in the atmosphere. There are two major roles that clouds play: they transport pollutants in the vertical; and they provide an additional media for chemical transformations to occur. The transport effects are discussed in this section.

Isaac et al. (1984) have conducted field studies on how clouds redistribute pollutants. They have shown that precipitating and non-precipitating clouds vertically transport significant amounts of pollutants out of the sub-cloud layer. They established that cloud (all types) are a prevalent feature of the atmosphere occurring 80 to 90 percent of the time in Ontario and Quebec. They also found that the Cloud Vertical Transport Ratio (VTR) (i.e., the amount of sub-cloud layer air pumped through clouds each hour) ranged from 10 to 30 percent in winter and 30 to 90 percent in the summer. These findings suggest that a significant amount of near surface air can be transported over long distances over time scales of several days by this process. Furthermore, these pollutants can be cycled through clouds several times.

The transport effects caused by an ensemble of clouds can be generally classified as: 1) the detrainment of cloud air into the cloud environment at the upper levels of clouds, which acts as an effective source of pollutants since cloud air originates mainly at lower levels where pollutant concentrations are higher; 2) the downwind transport of cleaner air from the upper levels to the lower levels by compensating subsiding motion in the cloud environment, which can act as an effective sink of pollutants; and 3) the recycling of air by clouds which leaves a column of air at the end of the cloud's life cycle that has a different (and often higher) concentration than the surrounding air and represents a pollutant source for the cloud layer.

Processes 1) and 3) are particularly important because they provide a mechanism to transport and release material at higher elevations. Not only can these materials at higher elevation be transported long distances, but the horizontal winds at these elevations can be quite different than those near the ground. Cho and Iribarne (1984) have presented the trajectories at various heights for parcels originating at Toronto, Canada (see Figure 3). As shown, the surface winds first moved the parcel in the WSW direction, and then in the SE direction during a 24-hour period. However, the 500 mb winds carried the air parcels eastward out over the Atlantic Ocean in less than 12 hours.

These processes are potentially very important in the long range transport of materials. However, their treatment in Eulerian models is currently either nonexistant or very primative. The difficulty in incorporating these processes into Eulerian long range transport models lies with the fact that these individual cloud processes occur on spatial scales much smaller than those resolved by the transport/chemistry model. For example, the horizontal scale of a cumulus cloud is about 10 kilometers or less. Furthermore, the fractional area covered by cumulus clouds in a synoptic scale weather system is usually of the order of a few percent. An additional problem is that the wind field data obtained from either routine meteorological observations or from dynamic meteorological models provide information only at the synoptic scale and provide no information about the air circulation on the cloud scale.

The incorporation of cloud venting processes into Eulerian long range transport models requires the development of parameterization techniques which relate the important processes to information on in-cloud properties (e.g., vertical velocity profiles, liquid water content, cloud height, etc.) and inputs on the amount and the size spectrum of the cloud population. The former inputs can be obtained from detailed cloud models

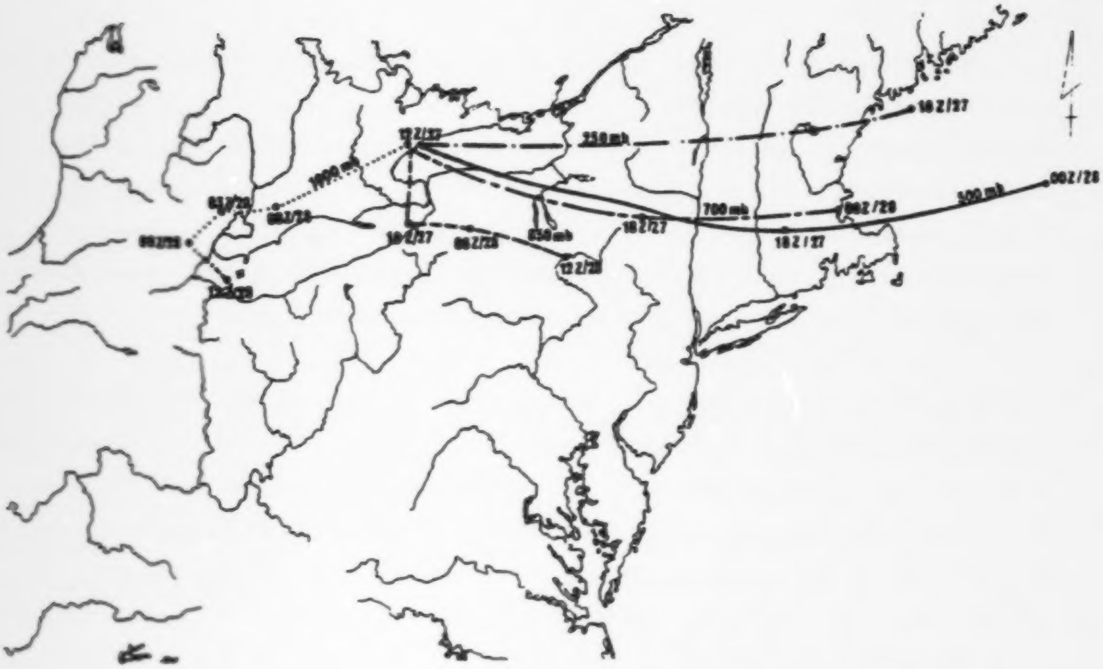
12Z/27
250 mb
18Z/27
1000 mb
00Z/28
500 mb
700 mb
00Z/28
18Z/27
18Z/27
850 mb
18Z/27
00Z/28
00Z/28
12Z/28
00Z/28
12Z/28

Figure 3. Air parcel trajectories originating from Toronto, Canada, 127, 27 July, 1982 (from Cho et al., 1984).

incorporating microphysical and chemical processes whereas the latter can be obtained by a variety of observational, diagnostic modeling, closure theory, and empirical relations techniques. However, each of these methods have their associated errors and uncertainties (cf, Cho and Iribarne, 1984). The development of such parameterizations is currently underway (cf, Cho and Iribarne, 1984; Gidel, 1983; and Ritter, 1983). These techniques will be discussed in more detail in the section on sub-grid scale processes.

2. Chemistry

The principal chemical species from the standpoint of acid deposition are NH_3, NH_4^+, H^+, SO_2, SO_4^{2-}, HNO_3, NO_3^-, and perhaps HCl and organic acids. However, the chemical cycles of these species are complex and highly coupled to one another. Furthermore these chemical cycles are highly dependent on the NO_x, hydrocarbon, and free radical chemistry of the troposphere. Therefore a chemical mechanism for acid species must involve the chemistry of photochemical oxidants and acid precursors.

The chemical processes are incorporated into the model framework through the chemical reaction term, R, in Eq. (4). This term involves both homogeneous gas phase chemistry, and heterogeneous processes. This term is also important mathematically because it introduces nonlinearity to Eq. (4) and provides a coupling between various species and various phases. As a result, Eulerian modeling involves the solution of a set of nonlinear coupled partial differential equations.

The chemical processes affecting the long range transport of pollutants are complex and involve photochemical, free radical, and aqueous phase reactions. It is generally not feasible to include all the possible reactions into a long range transport model due to computational and uncertainty considerations. Rather it is necessary to describe the chemistry in a manner that balances accuracy against the number of species and reaction pathways. In this section the major uncertainties and errors associated with the chemical processes are discussed.

a. Homogeneous chemistry

The important homogeneous gas phase chemical reactions affecting the distribution of pollutants on regional scales involve the interaction of the chemical cycles of sulfur, oxygen, nitrogen, hydrogen and carbon. The number of species within a particular group can be large, and therefore only the most important species can be included.

One important problem in selecting the chemical species and reactions to be included in a model involves the treatment of the organic and free radical species. Two basic approaches have been used to simplify the hydrocarbon chemistry. The surrogate mechanisms (cf, Graedel et al. (1976) and Dodge (1977)) treat organic species in a particular class, e.g., ole fins, by a representative member (e.g., propylene). The second approach uses chemical lumping where chemicals of similar structure and reactivity are grouped together in a single class (cf, Falls and Seinfeld (1978), Whitten et al. (1979)). The basic objective of this approach is to take advantage of the common features of the hydrocarbons and free radicals in order to minimize the number of species while at the same time maintaining detail for the inorganic reactions. The basic features of the various mechanisms can be found in the above citations and in McRae et al. (1982).

Each approach at simplifying the chemistry involves the testing of the proposed mechanism against chemical chamber studies. In so doing the models can be tuned to give the best response to the selected observations and give some confidence to further applications. However, it is a very difficult task to assess the error and uncertainties in the various simplifying assumptions, the choice of included reactions steps, and the various rate constants.

Insight into the errors of the different procedures can be obtained by comparing various schemes under common simulation conditions. This was done by Dunker et al. (1984). He compared four chemical schemes: a) the EPA mechanism (Durbin et al. 1975), and Dodge (1977a) which is a surrogate mechanism with detailed kinetics for butane, propane, formaldehyde and acetaldehyde; b) the FSM developed by Falls and Seinfeld (1978) which is a lumped mechanism with six organic classes representing alkanes, ethylene, higher alkenes, formaldehyde, higher aldehydes, and aromatics; c) the CB II mechanism of Whitten et al. (1980) which is a lumped mechanism where the carbon atoms are lumped into the five classes of alkane, ethylene, higher alkene, carbonyl, and aromatics; d) the ELSTAR mechanism developed by Lloyd et al. (1979) which is a lumped mechanism with a classification scheme similar to FSM.

The important findings of this study are:

1. Using identical simulation conditions, the four chemical mechanisms predict substantially different 1-hr average O_3 and PAN concentrations. The times necessary to reach the maximum concentrations also differ from mechanism to mechanism. The predicted maximum 1-hr averaged NO_2 concentrations are similar as are the times to the NO_2 maxima.

2. The calculated nonmethane hydrocarbon reductions necessary to meet the O_3 standard are very sensitive to the mechanism employed.

3. All mechanisms show NO_x inhibition of O_3.

4. Some of the differences between the calculated values are due to different assumptions on aldehyde photolysis rates and radical sources in the chamber.

An underlying uncertainty in the development of chemistry mechanisms lies in the fact that major reaction pathways are incompletely understood. For example, the NCAR Acid Deposition Model Chemistry Advisory Group has identified several key issues related to the formulation of chemical mechanisms for use in long range transport models (cf, Quarterly Report, EPA). The issues identified were: 1) What is the significance of the Criegee intermediates in acid generation?; 2) What are the major oxidation pathways for NO_x at night, and specifically what is the rate constant for the homogeneous reaction of N_2O_5 with H_2O?; 3) What are the major processes leading to the generation of organic acids in the troposphere?; 4) What is the extent of the aromatic peroxy radicals in the nitrate formation cycle?; and 5) What is the significance of the nighttime reactions of nitrate radicals with organic compounds?

Further uncertainties and errors enter into the reaction mechanism in the calculation of the extrapolation of rate constants measured in the laboratory, in the determination of the temperature dependence, in the determination of the photolytic rate constants, especially under conditions of high aerosol loadings or in the presence of clouds, and in the initialization and numerical simulation of the kinetic mechanism (these will be discussed in more detail in later sections).

b. Heterogeneous chemistry

It is becoming widely appreciated that heterogeneous processes involving gas-particle and gas-hydrometeor interactions play important roles in the atmosphere. However, there remain significant gaps in our basic understanding of the nature and importance of the various heterogeneous processes. Nonetheless, their potential importance is great and these processes are beginning to be treated in long range transport models.

Aqueous phase reactions involving species absorbed from the gas phase and those arising from the dissolution of particulate material represent important heterogeneous processes. Many of the important reactions and the associated errors and uncertainties for this process are analogous to those discussed for homogeneous chemistry. However, the uncertainties in the aqueous phase chemistry are perhaps larger than those in homogeneous chemistry because of the limited laboratory and field data available. The aqueous phase chemistry is further complicated by the various metal and carbon catalyzed reactions that can occur.

The key uncertainties in the aqueous phase chemistry involve the identification of the major S(IV) oxidation pathways, the identification of processes that generate nitric acid in solution, the quantitative aspects of organic acid generation in the liquid phase by OH-organic molecule reactions, the chemical mechanism for hydrogen peroxide formation in solution, the assessment of the importance of the reactions of free radicals transferred from the gas phase to the aqueous phase, and the determination of the solubility and other physical/chemical properties of free radical and other important atmospheric species. Detailed aqueous phase mechanisms have been formulated (cf, Graedel (1983), Chameides (1984)). Simulation results indicate that the aqueous phase chemical reactions are important sources of acidity in hydrometeors. However, the importance of the various aqueous phase reactions is sensitive to the assumptions regarding the gas absorption of the soluble species (especially OH and HO_2), the amount of liquid and the number and size of the dispersed droplets, and the ambient levels of the reactants. Results from a transport model which included detailed gas and liquid phase chemistry (Cho and Carmichael, 1984) have further indicated that the aqueous phase reactions are important and that they can lead to significant nonlinear relationships between ambient sulfate values and SO_2 emissions.

Another important heterogeneous process involves the deposition of gaseous species onto aerosol particles. This process can change the gas phase composition by preferentially removing species and can provide surfaces for heterogeneous chemical reactions. The deposition of gases to aerosol surfaces has been calculated for a Junge size distribution and Jaenicka residence time distribution by Luther and Peters (1982). Their results indicate that the heterogeneous rates of some species (e.g., HNO_3) could dominate known homogeneous processes. Calculations also suggest that the importance of heterogeneous removal of trace gases may vary diurnally and are coupled to those aerosol processes and meteorological factors which determine whether the aerosol is a solid or a liquid. However, quantifying the importance of this process will require measurements of the accomodation coefficients of various chemical species and chamber studies involving mixtures of gases and particles.

The formation of aerosol particles is important in long range transport models because a chemical species in particulate form may be deposited and transported at rates different than in the gaseous phase. The mechanisms of gas-to-particle conversion are complicated and are presently treated in a highly parameterized form in long range transport models (e.g., pseudo first order reactions). However, the rates of these reactions are large enough to significantly affect the gas phase concentrations of species such as SO_2, NH_3, and HNO_3.

One procedure for treating the aerosol formation is to use the assumption that the gas phase and the aerosol phase are in chemical equilibrium. This assumption has been used by Stelson and Seinfeld (1982) to develop a module for use in transport models. Preliminary calculations using a transport/chemistry model indicate that the aerosol equilibrium assumption is valid (Russel et al. (1983)), and that trends in the diurnal cycle of NH_3 and HNO_3 cannot be accurately modeled using pseudo first order chemical reactions (Chang, 1984).

3. Removal Processes

The processes of dry and wet deposition play an important role in the long range transport and redistribution of pollutants in the atmosphere. These processes also control to a large degree the source-receptor relationships.

a. Dry deposition

The dry deposition processes represent important pollutant sinks and can greatly affect the vertical distribution and subsequently the transport. For example, mass balances for SO_x calculated using an Eulerian transport/chemistry model indicate that over 24-hour periods the amount of SO_2 deposited exceeds the amount of SO_2 reacted to sulfate by nearly an order of magnitude, whereas the amount of sulfate deposited is similar to the amount of sulfate generated by reaction (cf, Carmichael and Peters, 1984).

The dry deposition process is included into the model analysis as the boundary condition to Eq. (4) at the bottom surface; i.e.,

$$K_{\alpha\alpha} \cdot \frac{\partial}{\partial z} \langle C_i \rangle = Q_i - V_{g,i} \langle C_i \rangle, \tag{5}$$

where $V_{g,i}$ is the dry deposition velocity of species i at the reference height of the bottom surface of the model, and Q_i is the surface source term. The dry deposition velocities are not fundamental quantities but rather are defined experimentally as

$$V_{g,i} = F_i/C_i(Z_r), \qquad (6)$$

where Z_r is the reference height and F is the downward flux of material. The relationship between V_g and the classical mass transfer coefficients has been discussed by Carmichael and Peters (1984).

The dry deposition velocities are influenced by both the transport of material to the surface and the interaction of the pollutant with the surface. Thus, the deposition velocities are dependent on meteorological factors (e.g., wind speed, stability, etc.), surface type (e.g., soil, grass, etc.), and the chemical and physical properties of the pollutant. Furthermore, due to both meteorological and physiological considerations the deposition velocity of a given point varies diurnally and seasonally. For example, the maximum daytime and nighttime dry deposition velocities may differ by an order of magnitude. Ignoring this diurnal variation and using a constant value may lead to large overpredictions of deposition during the nighttime and underpredictions during the daytime. This in turn can affect the spatial and temporal deposition distributions.

Models that predict temporal and spatial variations of dry deposition velocities have been developed for use in Eulerian models (cf, McRae (1983), Carmichael and Peters (1984)). These models estimate the aerodynamic and surface deposition resistances given observational meteorological and land use data, and take into account the reference vertical calculation height. However, these models are quite speculative because the deposition velocities of only a relatively few species at distinct locations have been determined experimentally. Furthermore, the field study data on the spatial and temporal distribution of dry deposited materials, that would enable the evaluation of these model treatments of dry deposition, are not available.

b. Wet deposition

As mentioned previously, cloud processes appear to be important in the long range transport of pollutants. Clouds can effect the large scale meteorology through latent heat release to the air and through the transport of momentum; they can affect the photolysis rates; they can transport pollutants to the lower troposphere and away from surface deposition, to the upper troposphere and into global circulations, and back to the boundary layer where they can be chemically modified or removed by deposition; they can enable aqueous phase chemical reactions to occur; they can organize small scale mesoscale convergent motions and transport pollutant material to cloud base; and they can remove gaseous and particulate pollutants. The chemistry and transport properties have been discussed in previous sections. The removal processes will be discussed briefly here.

The wet deposition of pollutants involves the interaction of pollutants with cloud water, rainwater, and ice, and can occur both in-cloud and below-cloud. Wet removal involves the basic gas absorption and aerosol capture processes which, in turn, are influenced by the microphysical processes that occur in-cloud. The wet removal process is incorporated into the model framework by term G in Eq. (4).

The major question regarding the wet removal process is how to treat this process in Eulerian long range transport models. Model studies using pseudo-first order formulations of wet removal coefficients have shown that wet removal processes can greatly affect the distribution and can contribute significantly to variability in calculated pollutant levels (cf, Thompson and Cicerone (1982), Carmichael et al. (1982)). However, the pseudo-first order removal rate constants (or scavenging coefficients) are complex functions of cloud water content, drop size, rainfall rate, ambient temperature, droplet pH, droplet age, and trace gas composition (cf, Carmichael and Reda (1982), Hong and Carmichael (1984)). Since cloud microphysical parameters are not routinely measured it is necessary to use cloud models to calculate the wet removal rate constants.

The coupling of long range transport models with cloud models is a very critical item that is just now being done. Preliminary calculations using STEM-II coupled with the PLUVIUS cloud model indicate the complexity of the removal processes in-cloud and also that both spatial and temporal variations occur within the clouds. These calculations also show that the wet removal process can: induce difficulties in the numerical simulation by increasing the stiffness of the problem in and near the cloud; necessitate the transport of clouds within the model so that the removal coefficients can respond to changes in liquid phase compositions and so that the materials can be redistributed during cloud evaporation and precipitation; and can influence the gas phase chemistry by perturbing the gas phase composition (by removal, evaporation, or precipitation) and reducing the photon flux.

The errors and uncertainties introduced by the various treatments of cloud processes are probably large but have not yet been quantified in the context of the model framework. The sub-grid scale aspects of this problem are discussed in Section 3.1.

C. Sources

An accurate knowledge of the temporal and spatial emission distributions for the primary pollutants and other important chemical species is necessary to simulate long range transport. In Eulerian models the emissions of each transported species must be specified as a function of position and time. Elevated sources enter into the model analysis through term S_i in Eq. (4) whereas surface sources enter through the boundary condition (i.e., Eq. (5)). The emissions must be resolved to the scale of the grid system used (e.g., horizontal grid sizes of $\sim$ 50 km), distributed at the effective source height, and show the important diurnal, seasonal, or annual variations. The availability of the necessary emission inventories and the treatment of elevated sources are discussed in this section.

1. Emissions inventories

Emission inventories are needed for SO_x, NO_x, HC, NH_3, particulate cations (Ca, Na, Mg, Mn, Fe), and perhaps CH1 and CO. The available anthropogenic source inventories are summarized in Table 2. The most complete inventories in the U.S. and Canada are available for SO_x and NO_x. However, there is still the need to prepare the inventories on smaller grid sizes and extend the area covered by the data base. One specific problem

TABLE 2

Summary of U.S.-Canadian Work Group 3B Data Bases.

1. U.S.-Canadian Work Group 3B Data Bases

   a. 1978 Data Base

      Pollutants: SO_x only

      Geography: National, U.S. and Canada--U.S.--major point-sources, county level area sources in the East, State areas sources for Western States. Canada--major point-sources and area sources in 127 km grids.

      Sources: All sources aggregated to 10 categories

      Time Frame: 1978

      (The U.S. portion of this data base was constructed from parts of 1 through 4 above to meet immediate needs for atmospheric modeling.)

   b. 1980 Data Base

      Pollutants: SO_x and NO_x

      Geography: National--U.S. and Canada--U.S.--State level totals. Canada--major point-sources and area sources in 127 km grids.

      Sources: All sources aggregated into six categories

      Time Frame: 1980

   c. Preliminary Estimates

      Pollutants: Primary Sulfates, VOC, Trace Metals

      Geography: U.S. and Canada--U.S.--State level. Canada--province level.

      Sources: All sources aggregated into major categories

      Time Frame: 1980

TABLE 2 (Continued)

2. Northeast Corridor Regional Modeling Project (NECRMP) Inventory (OAQPS)

Pollutants:	NO_x, VOC, CO
Geography:	14 Northeastern States plus D.C. All sources allocated to 20 x 20 km grid squares.
Sources:	All area and point-sources
Time Frame:	1979, 1980 allocated to hourly emissions

with the SO_x inventory is that the estimates of the primary sulfate appear to be very uncertain (cf, Goklany and Hoffnagle, 1984).

The Eulerian long range transport models require speciated hydrocarbon emissions. The emissions must be prepared in accord with the treatment of hydrocarbons in the chemical reaction module. If a lumping technique using six classifications is used then the emissions must be lumped in a similar way. Techniques to do this are available (cf, Novak and Sutherland, 1984), but the basic hydrocarbon emissions data is not available in all regions nor with the necessary resolution.

Preliminary studies of sensitivity of nitrate and sulfate to changes in reactive hydrocarbon emissions have been done using detailed gas phase mechanisms in langrangian models (cf, Samson (1982) and Seigneur et al. (1984)). Samson's results indicate that a 10% decrease in reactive hydrocarbon emissions results in a 7.5% reduction in ambient sulfate, 4% reduction of wet deposition of sulfate, and a 3% reduction in sulfate dry deposition, at a distance equivalent to 24 hours travel time. Seigneur's analysis for conditions typical of Los Angeles indicate that maximum simultaneous reductions in sulfate and nitrate could be obtained by reducing reactive hydrocarbons rather than reducing SO_2 and NO_x. Furthermore, studies including detailed liquid phase chemistry indicate that carbonyls are important in controlling free radical reactions in solution (cf, Adewuyi et al. (1984)). The emission of carbonyls may require specific attention.

The source inventories of particulate matter including calcium, sodium, magnesium, iron, maganese for industrial and nonindustrial anthropogenic sources as well as natural sources are important and are currently not available. In addition, the source inventories of NH_3 are also lacking. It is also important to recognize that the source inventory requirements to evaluate models against observational data differ from those for control strategy application. The sensitivity of model predictions to the resolution (temporal and spatial) of the emissions needs to be quantified.

2. Treatment of elevated sources

The height of the emission of pollutants is important and can have a large influence on the resultant ambient distribution. For example, when the release height is below the top of the mixing layer, the material can be readily mixed within a short transport distance. If the emissions are injected into the inversion the material can remain aloft for long periods of time and be effectively isolated from surface removal processes.

The most common procedure to treat elevated sources in Eulerian long range transport models is to add the emissions from a source into the grid cell at the effective stack height. However, this can lead to an overprediction of concentrations in the near source region. Procedures to distribute the elevated emissions on the basis of plume dispersion parameters have been developed (cf, McRae et al. (1982), Seigneur et al. (1983)). A comparison of three-dimensional model predictions using a detailed treatment of the point sources (including chemistry) with that where the emissions are simply dumped into the grid cell at the effective release height, indicate that for a 24-hr simulation of the St. Louis urban area the detailed treatment of point sources did not notably affect model predictions of O_3 and NO_2 air quality (Seigneur et al., 1983).

The errors associated with grid representation of point sources have also been evaluated by Karamchandani and Peters (1983). They found that for an inert pollutant that the ground level concentrations predicted using an equivalent volume source were in close agreement to the point source values at downwind distances greater than 10 km.

Detailed treatment of the point sources may be important when the individual source-receptor relationships are desired. However, alternative approaches may be possible.

D. Numerics

The governing equation for Eulerian long range transport models (i.e., Eq. (4)) represents a set of coupled, time dependent partial differential equations. The coupling enters in through the reaction and removal terms and involves the gas and the dispersed hydrometeor phases. The reaction term also introduces nonlinearities into the equations. Furthermore, the reaction and removal terms can make the equations very stiff, convection processes usually dominate horizontal (and sometimes vertical) transport, the boundary conditions are mixed, and the topographical features make the domain of interest irregular. These factors make the numerical solution of Eq. (4) difficult.

There are many methods available for solving atmospheric transport problems. The methods available can be broadly classified into the categories of finite-difference schemes, variational methods, pseudo-spectral methods, and particle-in-cell techniques. The methods can be further classified as explicit or implicit, depending on whether each succeeding integration step is direct (explicit) or requires the simultaneous solution of the equations (implicit). In general, implicit methods are computationally more difficult than explicit methods, but they frequently are numerically stable over larger ranges of spatial and temporal step sizes.

The most troublesome problems involve dissipation, dispersion, and aliasing. Numerical dissipation errors, which can be introduced when first-order numerical approximations are used, tend to smooth initially peaked distributions. Dispersion is common to all methods and arises from the approximation of the advection terms. In the numerical solution, all Fourier components lag the true solution, and each wave number component travels with a different speed. This is unlike the real solution where all components travel with the same speed. This lagging causes the different Fourier components to spread apart, or disperse, as the numerical solution proceeds. This error is larger for the shorter wavelengths. Aliasing is associated with energy exchange between Fourier components and will occur in problems involving spatially varying wind fields. The Fourier components interact in such a way that energy cascades from long wave-lengths to shorter ones; if no dissipative mechanism is present to remove the energy from the shortest wavelength, the energy will flip over and reappear in the long wavelengths. The many numerical techniques available reflect different attempts to decrease or compensate these errors.

The selection of a numerical technique for a specific application must be based on a number of considerations, including numerical stability, accuracy, non-negativity of computer concentrations, computer storage requirements, computing time requirements, and adaptability of the method to the solution of the governing equations. Fortunately, a number of performance tests have been conducted that compare directly many of the numerical techniques available (Carmichael et al. (1980), Crowley (1968), Pepper et al. (1980)). These comparison studies indicate that there are many methods that can be used and each has its own strengths and weaknesses. One important problem is that the methods are generally evaluated using simple flow systems. However, modifications taken to improve model performance in these situations (e.g., filtering, upwinding, etc.) may not have the same effect on performance when used in complex flows.

The numerical solution of the reaction and removal terms requires further attention. The solution of gas phase chemistry in long range transport models has been studied intensely. It is recognized that the detailed treatment of the gas phase chemistry can introduce extreme stiffness into the problem (the dynamic range of the eigen values of the Jacobian can exceed 10^{12}). One way of reducing the stiffness of the problem is to use the pseudo steady state approximation. The main difficulties with this technique is the identification of those species which can be treated in this way and the determination of the time after which the approximation is valid.

Similar problems arise in the numerical treatment of wet removal and liquid phase chemistry. For example, the gas absorption process can cause very sharp gradients in the soluble species profiles, and the dissociation reactions are extremely fast. The numerical solution is complicated by the coupling of the mass transfer and the liquid phase chemistry. The use of vapor-liquid equilibrium assumptions can reduce the stiffness. However, this must be invoked carefully because the presence of liquid phase chemistry can affect the rate at which equilibrium is approached. For example, the use of the equilibrium assumption for HNO_3, OH and HO_2 may overpredict the liquid concentrations by an order of magnitude.

The most critical factor in the numerical solution of Eq. (4) may be the assurance that the proper time-steps are used. The source distribution, the convective scales, the gas and liquid phase chemistry, and the wet removal process can all influence the proper time-step selection.

PROBLEMATICS

The errors and uncertainties associated with the various components of Eulerian long range transport models have been discussed in the previous section. However, there are additional areas which have received relatively little attention that also affect model performance. These topics will be discussed in this section.

A. Sub-Grid Scale Processes

There are a number of important problem areas related to sub-grid scale processes that are readily identifiable. Examples include these chemical processes that occur within plumes which are smaller than the grid elements (e.g., point sources, urban plumes, cloud vented plumes), the affects of the turbulence on the near source chemistry, and the treatment of cloud processes.

The sub-grid-scale chemistry processes arise due to the fact that the model (i.e., Eq. (4)) calculates the chemical rates based on the cell averaged concentrations, whereas the reaction rates depend physically on the actual concentrations in the plume.

An upper bound on the error associated with the calculation of the mass of product formed by a pollutant undergoing first order kinetics emitted from a point source was evaluated by Lin (1980). He calculated the mass converted in a fixed time using a Gaussian plume model and an instantly mixed box model the size of one grid element. He found that the treatment where the mass is uniformly mixed throughout the cell over-estimated the conversion relative to that calculated by the plume model by a factor of two when the source was at the upwind boundary, a factor of four with the source at the center of the element, and over an order of magnitude as the source approaches the downwind boundary. The actual reaction rates are also influenced by the initial mixed state of the reactants. The pollutants can be premixed as in emissions from the same source or segregated as in the case of distinct sources.

A related problem involves the affect of turbulence on the chemical reactions. As mentioned in the discussion leading to Eq. (4), the decomposition of the concentration field into deterministic and random components leads to the introduction of correlation terms into the reaction rate, e.g., $k(\bar{A}\,\bar{B} + \overline{a'b'})$. A positive correlation can increase the reaction rate and a negative correlation can decrease the rate.

The turbulence can affect the near source chemistry (cf, Donaldson and Hilst (1972), Carmichael and Peters (1981)). More recently a study of an NO_x plume emitted into background containing O_3 undergoing turbulent mixing derived from the Yamanda-Mellor boundary layer model has shown the three dimensional nature of mixing-limited chemistry (Karamchandani and Peters, 1984). The calculated photostationary state parameter ($\lambda = k_1[NO][O_3]/k_2[NO_2]$) is substantially less than one in the near source region, but depending on the turbulent mixing can more or less rapidly approach unity. The affect of these chemical processes on the predicted distribution fields resulting from the long range transport of pollutants requires quantification.

Another important sub-grid-scale problem is the representation of transport and removal by clouds. Difficulty in treating cloud processes arise because clouds may occupy only a small volume of a grid cell at any particular time. One method for parameterizing cloud transport is to treat it as an enhanced vertical turbulent diffusion process by using a high eddy diffusivity (100-1000 m^3/s). However, Gidel (1983) has shown that vertical diffusion alone is inadequate to account for the redistribution of pollutants due to the presence of a convective cloud field.

Recently a number of methodologies have been presented to treat the affects of cloud ensembles (cf, Gidel (1983), Ritter (1984), Cho and Iribarne (1984)). In these models, cloud transport processes are modeled in terms of the cloud mass flux.

For example, (cf, Cho and Iribarne (1984)), the mean grid cell concentration in another ensemble of cumulus cloud can be written

$$\begin{aligned} \frac{\partial \langle C_i \rangle}{\partial t} + \frac{\partial}{\partial x_\alpha} (U_\alpha \langle C_i \rangle &= \frac{\partial}{\partial x_\alpha} (K_{\alpha\alpha} \frac{\partial \langle C_i \rangle}{\partial x_\alpha} \\ &+ (1-\Sigma) R_i + S_i - G_i + \frac{\Sigma}{\gamma} (C_{ic} - \langle C_i \rangle \\ &- (\frac{\partial M_c}{\partial z}) (C_{ib} - \langle C_i \rangle) + M_c \frac{\partial \langle C_i \rangle}{\partial z} \end{aligned} \tag{7}$$

where Σ represents the fraction of the volume occupied by cumulus cells, γ is the mean life span of the cumulus clouds, M_c is the cloud mass flux, C_{ic} is the in-cloud pollutant mixing-ratio and C_{ib} is the concentration of the entrained air (i.e., $C_{ib} = \langle C_i \rangle$ during entrainment and $C_{ib} = C_{ic}$ during detrainment). Term 1 represents a source of gas phase material due to the evaporation of clouds, Term 2 represents the increase in mixing ratio due to detrainment of cloud air (note that this term is zero for entrainment) and Term 3 represents the affect of the compensating downward motion in the cloud environment.

The use of this parameterization requires the estimation of the cloud mass flux. This can be done by use of cloud models (cf, Gidel (1983), Cho and Iribarne (1984)) or it can be estimated from satellite imagery (Ritter, 1984). An example of the effect of the use of this parameterization on calculated vertical profiles is shown in Figure 4 (cf, Gidel (1983)). It is important to note that the including cloud transport curve cannot be produced with use of an enhanced eddy diffusivity. Also, Ritter (1984) has found that in the case of O_3, the effects of cloud venting can be more important than in situ chemical production on the regional scale. These preliminary results suggest that cloud processes must be included in any meaningful analysis of long range transport.

B. Model Initialization

Eulerian models require initial and boundary concentrations of all calculated species at each grid point. The specification of these concentrations is difficult since for a given historical period observations of only a few species at a limited number of discrete locations are available. Furthermore, most of the observations are at ground level and very little upper air information is available. The initial conditions are important because they will determine the chemistry that occurs (at least during the beginning of a simulation). Furthermore, the gas phase chemistry can be quite sensitive to initial conditions (e.g., O_3 production is sensitive to the levels of NO_x and HC and also to their ratio). The problem of initialization is present in all model calculations but is particularly important in long range transport models because the vertical domain of interest is large.

A common way of treating this problem is to make the best estimates for initialization and then run the model for several days before the actual simulation period. This seasoning is done to allow the initial conditions to become self consistent and thus to minimize the affect of the assumptions about the initial conditions. However, the memory of long range transport models and the sensitivity of the calculated pollutant distributions to the initial conditions remains to be evaluated.

The specification of the boundary conditions is a similar problem. When there is inflow at a boundary, the boundary condition requires the concentration of the incoming air. Here too, the concentrations must be specified from sparse data. This problem may be more complicated since season

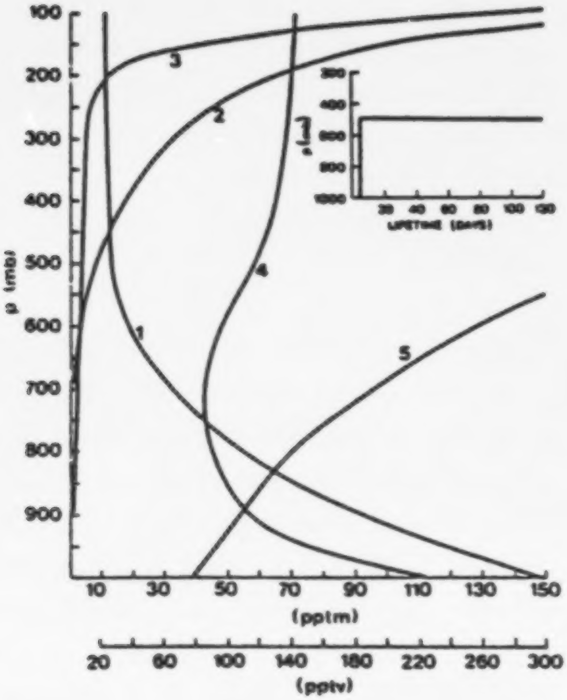

Figure 4. The effect of cloud treatment on vertical profiles. Profile 1 results from including a surface source plus large scale transport only; Profile 2 results from a stratospheric source and large scale transport only; Profile 3 results from a stratospheric source plus large scale and cloud transport; Profile 4 results from a surface source plus large scale and cloud transport; and Profile 5 results from a stratospheric NO_x source equal in magnitude to the NO_x source at ground plus large scale and cloud transport. (From Gidel (1983)).

ing simulations will provide no information regarding the history of air mass before entering the model region.

C. Model Evaluation

As indicated by the discussions to this point, there are errors and uncertainties associated with every component of long range transport models. However, the utility of a model is determined by its ability to satisfactorily describe the concentration dynamics occurring in the model domain. The evaluation of the performance of the model is thus an important aspect of model development. However, the evaluation of complex models is difficult. It involves an assessment of the model validity (i.e., the correctness of the model in its representation of the basic chemistry and physics) and the comparison of the model predictions and observations.

The methodology of the evaluation of complex models has not received adequate attention. One problem involves the selection of realistic goals for model performance. The performance criteria must take into account that models predict volume averaged quantities whereas observations are at specific points, and the uncertainties associated with the aerometric and the input data. Furthermore, it is important, but extremely difficult, to determine whether discrepancies between prediction and observations are due to errors in the input data, the model formulation or the observations.

The statistical analysis of the model predictions plays an important role in model evaluation. This subject has received considerable attention. An American Meteorological Society workshop has identified three basic classes of performance measures (cf, Fox (1981)): 1) analyses based on observed and predicted concentration field values paired for particular locations and times; 2) examinations of the ability of the model to predict peak concentrations; and 3) frequency distributions of the unpaired (in time) observed and predicted concentration values. However, no formal standards have been set as to what constitutes acceptable performance.

The systematic improvement of model predictions requires the assessment of both the uncertainties associated with the model parameters (e.g., emissions, meteorological factors, rate constants, initial conditions, etc.), and the sensitivity of the model prediction to variations in these parameters. Sensitivity analysis techniques suitable for use in long range transport models are being developed (cf, Rabbitz (1981), Tilden and Seinfeld (1982)). These techniques can provide important insights into model behavior. For example, Tilden and Seinfeld (1982) have applied sensitivity analysis to a photochemical air pollution model and have shown that: 1) predicted NO, NO_2, RHC and O_3 concentrations were relatively insensitive to uncertainties in the values of relative humidity, vertical turbulent diffusivity, and deposition velocity; 2) predicted concentrations were most sensitive to uncertainties in mixing layer height, photolysis intensity, initial conditions and emission intensity, and the relative importances varied during the course of the day; and 3) predicted ground-level concentrations are more sensitive to assumed O_3 concentrations aloft than to assumed RHC and NO_x concentrations aloft.

The evaluation and the improvement of model performance is also dependent of the availability of observational data. Ideally the model performance should be evaluated in terms of the most important species. For example, the OH concentrations in the gas phase and the liquid phase play an important role in the atmospheric cycles of SO_x, NO_x, and HC. However, there are very few measurements available. The development of data bases for such critical species would be extremely beneficial.

CLOSURE

The basic errors and uncertainties associated with Eulerian long range transport models have been discussed in terms of model formulation, input data, and model evaluation. To date, the trust of the modeling activity has been in the development of complex models and not in the quantification of errors. I feel that our understanding of the basic transport, chemical and removal processes, and our modeling experiences and capabilities (including computer resources) are such that scientifically credible models can be developed. However, since these model, by necessity, must include chemical, dynamic and thermodynamic parameterizations, they can only approximate real behavior. The degree of applicability of these models rests on the results of model evaluation studies.

The quantification of the errors and uncertainties in the model and the design of a methodology for model evaluation, including obtaining meaningful data sets for the evaluation, are critical steps in determining the utility of and the improvement of long range transport models.

REFERENCES

Adewuyi, Y.G., S-Y Cho, R-P Tsay and G.R. Carmichael (1984). Importance of Formaldehyde in Cloud Chemistry. **Atmos. Environ.**, 18:2413-2420.

Blumenthal, D.L., J.A. McDonald, W.S. Keifer, J.B. Tommerdahl, M.L. Seager and J.H. White (1984). Three-Dimensional Pollutant Distribution and Mixing Layer Structure in the Northeast U.S., Summary of Sulfate Regional Experiment (SURE) Aircraft Measurements. **Atmos. Environ., 18**:733-750.

Carmichael, G.R., T. Kitada and L.K. Peters (1980). Application of a Galerkin Finite Element Method to Atmospheric Transport Problems. **Computers and Fluids, 8**:155.

Carmichael, G.R., T. Kitada and L.K. Peters (1983c). The Effect of In-Cloud Scavenging on the Transport of Gas Phase Reactions of SO_x, NO_x, HC_x, H_xO_y and OÐ Compounds. **International Symposium on Precipitation Scavenging, Dry Deposition and Resuspension**, Elsevier Science Publishing Co., 10 pages.

Carmichael, G.R. and L.K. Peters (1981). Application of Mixing-Reaction in Series Model for Simultaneous Mixing and Chemical Reaction - NO_x-O_3 Plume Chemistry. **Atmos. Environ., 15**:1069.

Carmichael, G.R. and L.K. Peters (1984). An Eulerian Transport/ Transformation Removal Model for SO_2 and Sulfate: Part I - Model Development. **Atmos. Environ., 10**:937-953.

Carmichael, G.R. and L.K. Peters (1984). An Eulerian Transport/ Transformation Removal Model for SO_2 and Sulfate: Part II - Model Calculation of SO_x Transport in the Eastern United States. **Atmos. Environ., 12**:953-967.

Carmichael, G.R. and M. Reda (1982). Non-Isothermal SO_2 Absorption by Water Droplets - The Effects of Precipitation Intensity, Sulfate Aerosol Scavenging and Aqueous S(IV) Oxidation. **Atmos. Environ., 12**: 2905-2915.

Chameides, W.L. (1984). The Photochemistry of a Remote Marine Stratiform Cloud. **J. Geophys. Res.**, **89**:4739-4756.

Chang, Y.S. (1984). A Numerical Investigation of the Formation of Ambient NHđNOĐ Aerosol. M.S. Thesis, University of Iowa.

Crowley, W.P. (1968). Numerical Advection Experiments. **Mon. Weather Rev.**, **96**:1-11.

Cho, H-R, J.V. Iribarne, J.E. Grabenstetter and Y.T. Tam (1984). Effect of Cumulus Cloud Systems on the Vertical Distribution of Air Pollutants. **In**: The Meteorology of Acid Deposition, P.J. Samson (Ed.), APCA.

Daum, P.H., S.E. Schwartz and L. Newman (1983). Studies of the Gas and Aqueous Phase Composition of Stratiform Clouds. **In**: Precipitation Scavenging, Dry Deposition and Resuspension, W.G.N. Slinn (Ed.), Elsevier.

Dickerson, M.H. (1978). MASCON - A Mass Consistent Atmospheric Flux Model for Regions with Complex Terrain. **J. Appl. Meteor.**, **17**:241-253.

Dodge, M.C. (1984). Combined Use of Modeling Techniques and Smog Chamber Data to Derive Ozone-Precursor Relationships. EPA-60013-77-001b, Research Triangle Park, NC.

Donaldson, C. and G.R. Hilst (1972). Effect of Inhomogeneous Mixing on Atmospheric Photochemical Reactions. **EST**, **6**:812-816.

Dunker, A.M., S. Kumar and P.H. Berzins (1984). A Comparison of Chemical Mechanisms Used in Atmospheric Models. **Atmos. Environ.**, **18**:2, 311-321.

Durbin, P.A., T.A. Hect and G.Z. Whitten (1975). Mathematical Modeling of Simulated Photochemical Smog. EPA-650/4-75-026.

Falls, A.H. and J.H. Seinfeld (1978). Continued Development of a Kinetic Mechanism for Photochemical Smog. **EST**, **12**:1398-1406.

Fox, D. (1981). Judging Air Quality Model Performance. **Bull. Amer. Meteor. Soc.**, **62**, 599-509.

Gidel, L.T. (1983). Cumulus Cloud Transport of Transient Tracers. **J. Geophys. Res.**, **88**:6587-6599.

Goodin, W.R., G.J. McRae and J.H. Seinfeld (1979). An Objective Analysis Technique for Constructing Three-Dimensional Urban-Scale Wind Fields. **J. Appl. Meteor.**, **11**:98-108.

Goklany, I.M. and G.F. Hoffnagle (1984). Emission of Estimates as a Problem in Acidic Deposition Modeling. **In**: The Meteorology of Acid Deposition, P.J. Samson (Ed.), APCA.

Graedel, T.E., L.A. Farrow and T.A. Weber (1976). Kinetic Studies of the Photochemistry of Urban Troposphere. **Atmos. Environ.**, 10:1095-1116.

Graedel, T.E. and C.J. Weschler (1983). Chemistry Within Aqueous Atmospheric Aerosol and Raindrops. **Rev. Geophys. Space Physics**, **19**: 000-000.

Hong, M.S. and G.R. Carmichael (1983). An Investigation of Sulfate Production in Clouds Using a Flow-Through Chemical Reactor Model Approach. J. **Geophys. Res.**, **88**:10733-10744.

Isaac, G.A., P.I. Joe and P.W. Summers (1984). The Vertical Transport and Redistribution of Pollutants by Clouds. **In**: The Meteorology of Acid Deposition, P.J. Samson (Ed.), APCA.

Karamchandani, P. and L.K. Peters (1983). Analysis of the Error Associated with Grid Representation of Point Sources. **Atmos. Environ.**, 17:927-934.

Lamb, R.G. and J.H. Seinfeld (1973). Mathematical Modeling of Urban Air Pollution. **ES&T**, 7:253-261.

Lewellen, W.S. and M. Teske (1975). Turbulence Modeling and Its Application to Atmospheric Diffusion. Part I: Recent Program Development, Verification and Application. EPA/C00/4-75/0169.

Lin, C. (1980). Regional Scale Pollutant Transport Model. M.S. Thesis, University of Iowa.

Lloyd, A.C., F.W. Lurmann, D.K. Godden, J.F. Hutchins, A.Q. Eschenroeder and R.A. Nordsieck (1979). Development of the ELSTAR Photochemical Air Quality Simulation Model and Its Evaluation Relative to the LARPP Data Base. P-5287-500, ERT, Concord, MA.

Luther, C.J. and L.K. Peters (1982). The Possible Role of Heterogeneous Aerosol Processes in the Chemistry of CH_4 and CO in the Troposphere. In: Heterogeneous Atmospheric Chemistry, D.R. Schryer (Ed.), Geophsyical Monograph 26, AGU.

McRae, G.J., W.R. Goodin and J.H. Seinfeld (1982). Mathematical Modeling of Photochemical Air Pollution. EQL Report No. 16, C.I.T.

Mueller, S.F. (1964). Analyses of Errors in the Estimation of Wind Vectors for Medium/Long Range Air Pollutant Transport Processes. In: The Meteorology of Acid Deposition, P.J. Samson (Ed.), APCA, 274-289.

Pepper, D., E. Cooper and A. Baker (1980). An Investigation of Multi-Dimensional Computational Models for Calculating Pollutant Transport. In: Development in Theoretical and Applied Mechanics, J.E. Stoneking (Ed.), 10, 397.

Rabitz, H. (1981). Chemical Sensitivity Analysis Theory With Application to Molecular Dynamics and Kinetics. **Comp. and Chem.**, 5:167-180.

Reisinger, L.M. and S.F. Mueller (1983). Comparison of Tetroon and Computer Trajectories. **J. Climate and Appl. Meteor.**, 22:664-672.

Reynolds, S.D., P.M. Roth and J.H. Seinfeld (1973). Mathematical Modeling of Photochemical Air Pollution - I. Formulation of the Model. **Atmos. Environ.**, 7:1033-1061.

Ritter, J.A. (1984). The Determination of Cloud Base Mass Flux and the Vertical Redistribution of a Conservative Tracer. In: The Meteorology of Acid Deposition, P.J. Samson (Ed.), APCA, 177-189.

Russell, A.F., G.J. McRae and G.R. Cass (1983). Mathematical Modeling of the Formation and Transport of NH_4NO_3 Aerosol. **Atmos. Environ.**, 17:949.

Samson, P.J. (1982). On the Linearity of Sulfur Dioxide to Sulfate Conversion in Regional Scale Models. Prepared for the Congressional Office of Technology Assessment, June.

Seigneur, C., P. Saxena and P.M. Roth (1984). Computer Simulations of the Atmospheric Chemistry of Sulfate and Nitrate Formation. **Science**, 225:1028-1029.

Seigneur, C., J.W. Tesche, P.M. Roth and M-K Liu (1983). On the Treatment of Point Source Emissions in Urban Air Quality Modeling. **Atmos. Environ.**, 17:1655-1676.

Sheih, C.M. (1984). An Evaluation of Wind Field Interpolation Schemes Used in Studies of Regional-Scale Pollutant Transport. In: The Meteorology of Acid Deposition, P.J. Samson (Ed.), APCA, 324-346.

Shipley, S.T. and E.V. Browell (1984). Airborne LIDAR: Potential for Mixed Layer Measurements and Observations of Long Range Transport. In: The Meteorology of Acid Deposition, P.J. Samson (Ed.), APCA, 140-166.

Stelson, A.W. and J.H. Seinfeld (1982). Relative Humidity and Temperature Dependence of the Ammonium Nitrate Dissociation Constant. **Atmos. Environ.**, 16:993.

Tilden, J.W. and J.H. Seinfeld (1982). Sensitivity Analysis of a Mathematical Model for Photochemical Air Pollution. **Atmos. Environ.**, **16**: 1357-1364.

Thompson, A.M. and R.J. Cicerone (1982). Clouds and Wet Removal as Causes of Variability in Trace-Gas Compositino of the Marine Troposphere. **J. Geophys. Res.**, **87**:8811-8826.

Whitten, G.Z., H. Hogo, M.J. Meldgin, J.P. Killus and P.J. Bekowies (1979). Modeling of Simulated Photochemical Smog with Kinetic Mechanisms. Vol. I and II. EPA-600/3-79-001a, 718 p.

Yamada, T. and G.L. Mellor (1975). A Simulation of the Wangara Atmospheric Boundary Layer Data. **J. Atmos. Sci.**, **32**:2309.

CHAPTER III

SOURCES OF UNCERTAINTY IN LAGRANGIAN LONG RANGE TRANSPORT MODEL CALCULATION

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INTRODUCTION

I have been asked to discuss sources of uncertainty in Lagrangian long range transport model calculation. It is unavoidable however, that most of the points raised on the subsequent pages also will be relevant for Eulerian models. After all, the Lagrangian and the Eulerian technique are just two different ways of integrating the same basic equation.

In the discussion I have attempted to extract some information from simple analytical solutions, which I feel are related more to the Lagrangian approach than to Eulerian numerical techniques.

UNCERTAINTY IN TRAJECTORY POSITIONS

A. Trajectories and Instantaneous Plumes

A good way of investigating this question is to compare paths of tetroons with trajectory positions. Such data are presented for example in Clarke et al. (1983). The data were from USEPA field programmes. Figure 1 shows the standard deviation σ_ε of the distance between the tetroon and a diagnostic trajectory calculated by the NOAA ARL ATAD model (Heffter, 1980). Of the three trajectory models investigated, this model performed best on the average.

After three hours travel time, σ_ε is approximately 25 km, and after 21 hours about 200 km. This probably gives a good indication of the uncertainty of trajectories using current state-of-the-art techniques and meteorological input data. The uncertainty is approximately five times larger than the growth of an instantaneous plume as given by Carras and Williams Williams (1981), and shown in Figure 1. The uncertainty is also substantially larger than theoretical calculations of plume growth due to the combined effect of wind shear and vertical diffusion (Taylor, 1982) and than the material on plume growth presented by Gifford (1982). The two latter investigations give similar growth rates. Observations show that in some cases, plume growth is considerably slower. An observation from a UK plume study over the North Sea is shown in Figure 1 (Clark et al., 1983).

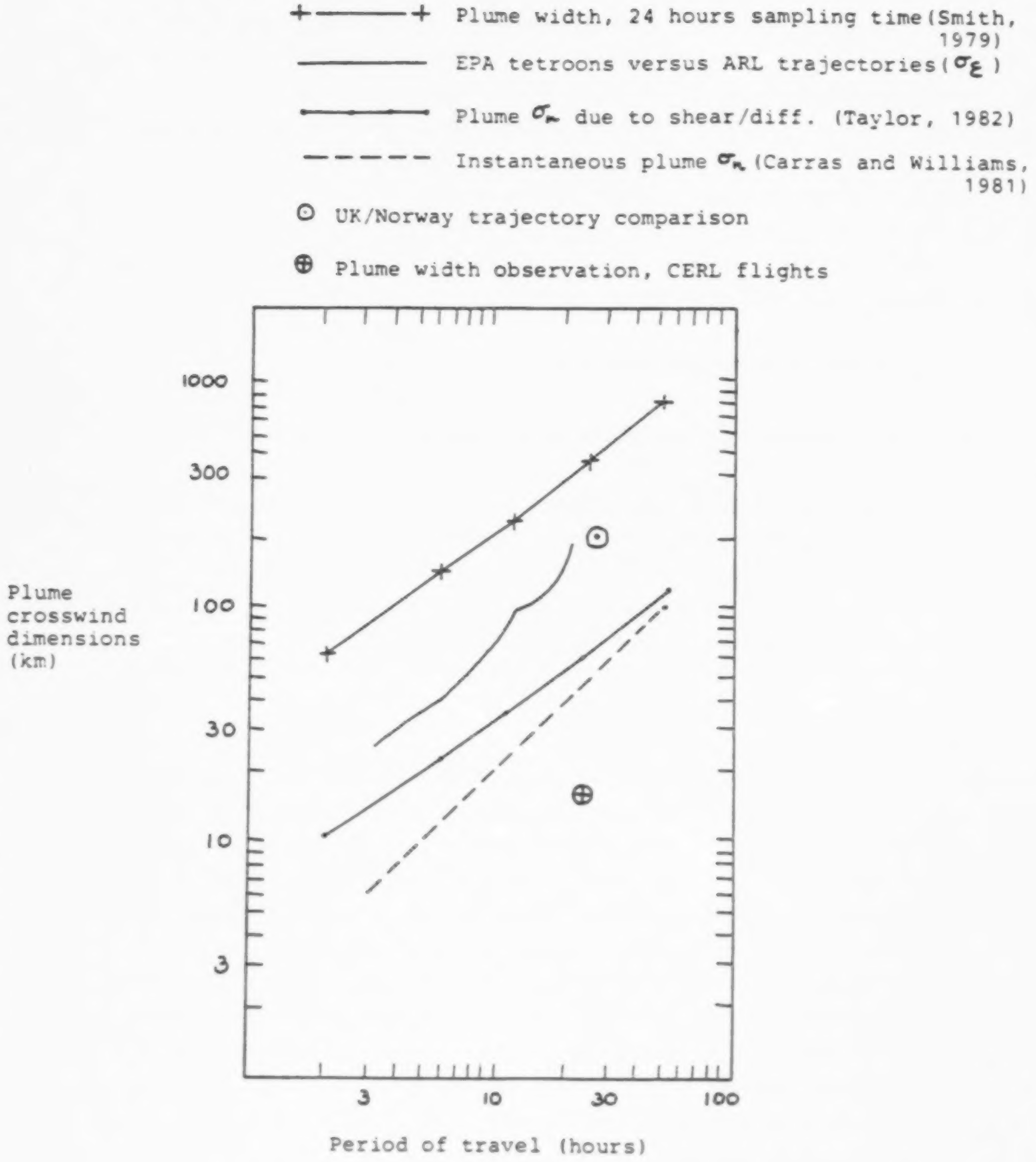

Figure 1. Horizontal dispersion characteristics.

A comparison between two different types of trajectories (surface geostrophic vs. 850 mb) after 1000 km transport (OECD, 1977), shows that their crosswind position difference is roughly comparable to σ_{ε}. This result is also plotted on Figure 1.

At present, we therefore have the following situation:

a) The uncertainty of a trajectory position, measured by the standard deviation between trajectory and tetroon positions is roughly five times larger than the crosswind standard deviation of an instantaneous plume.

b) the difference between different types of calculated trajectories that are reasonably well suited for transport calculations, is comparable to the difference between a calculated and a "real" (tetroon) trajectory.

B. The Effect of Averaging Time

If the problem is to calculate, say, daily average concentrations of a primary pollutant, then one should look at how accurately one can determine the position of a 24-hour time-average plume. Data on the crosswind dimension of such a plume taken from Smith (1979) is also shown in Figure 1. Clearly, the plume width in this case is considerably larger than the uncertainty of a trajectory position. This will be even more so for longer averaging times. Long-term (monthly, annual) concentration and dry deposition patterns therefore depend mainly on the trajectory path statistics and emission distribution, the uncertainty of individual trajectories being unimportant.

UNCERTAINTY IN CONCENTRATION AND DRY DEPOSITION DUE TO UNCERTAINTY IN DEPOSITION VELOCITY

A. Sensitivity of Concentration of a Primary Pollutant

The dependence of the concentration or dry deposition of a primary pollutant, as for example sulphur dioxide, on the deposition velocity, can be conveniently estimated using a simple statistical model for long-term dispersion (Rodhe, 1972). Consider dispersion of sulphur dioxide from a point source of strength Q within a sentor spanning an angle θ. The long-term average concentration q due to this source is

$$q = \frac{QT}{\theta hr} \cdot \frac{1}{r} \exp\left(-\frac{r}{u}\left(\frac{v_d}{h} + k_t + k_w\right)\right) \tag{1}$$

where r is the distance from the source, t is the time in which the wind at the source lies within the sector, u is an average wind-speed within the sector, h is an average mixing height, and k_t and k_w are average rates for transformation to sulphate and dry deposition, respectively. Differentiation of (1) with respect to v_d gives

$$\frac{dq}{q} = -\frac{r}{uh}\, dv_d \tag{2}$$

Note that (2) is valid even if we do not specify the functional form of the factor in front of the exponential function in (1).

In case we have a constant error dv_d in the deposition velocity, the resulting relative error dq/q in the concentration will increase linearly with travel time r/u. For $h = 10^3$ m and $dv_d = 10^{-2}$ ms^{-1} (i.e., a relatively large error), the resulting error in the concentration is 50% after a travel time of about half a day.

B. Sensitivity of Dry Deposition

Using the same model, the long-term average dry deposition D(r) is

$$D(r) = \frac{Qv_d t}{\theta hu} \cdot \frac{1}{r} \exp\left(-\frac{r}{u}\left(\frac{v_d}{h} + k_t + k_w\right)\right) \tag{3}$$

Differentation of (3) with respect to v_d gives

$$\frac{dD}{D} = (1 - \frac{rv_d}{hu}) \frac{dv_d}{v_d} \qquad (4)$$

relating the realtive change in the deposition velocity to the relative change in dry deposition.

Figure 2 shows $(1 - \frac{rvd}{hu})$ as a function of r and v_d with $h = 10^3$ and u = 10 m/s. For $rv_d = hu = 10^4\ m^2\ s^{-1}$, a small change in v_d gives no change in D. This is because an increase in v_d is compensated by a resulting decrease in the concentration. If v_d is 1 cms^{-1}, as for sulphur dioxide, then $|\frac{dD}{D}| < 0.5\ |\frac{dv_d}{vd}|$ from $r \simeq 500$ km to $r \simeq 1500$ km. On the regional scale, therefore, the dry deposition pattern is only moderately sensitive to the deposition velocity assumed for sulphur dioxide. In a way this is fortunate, since v_d for sulphur dioxide by no means is constant, but appears to vary between a few mms^{-1} up to about two cms^{-1}, depending on atmospheric turbulence and surface conditions.

WHAT FACTORS DETERMINE THE WET DEPOSITION PATTERN?

A pollutant may be incorporated into a raindrop in many ways. Pollution particles may act as condensation nuclei. Gases may diffuse into liquid

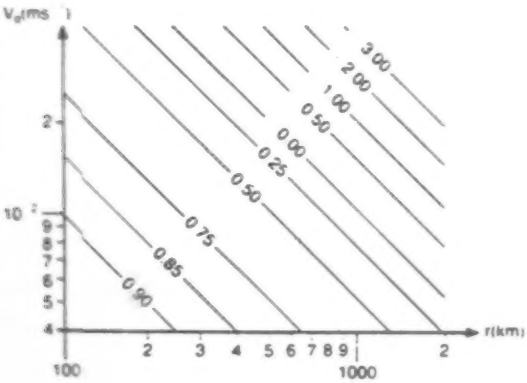

Figure 2. $(1 - \frac{rv_d}{hu})$ as a function of v_d and r, for $h = 10^3$ m and u = 10 m/s. For further explanation see text.

droplets, and be subject to chemical reactions in the liquid phase allowing for inclusion of additional gas. The rates involved vary widely from one precipitation event to the next, depending on cloud characteristics. A reflection of this complex situation is the variety of wet deposition rates that can be inferred from field experiments. For sulphur, however, there seems to be a broad consensus that its removal during precipitation is rapid with a characteristic time scale of the order of one hour.

The long-term average wet deposition pattern depends of course not only on the rate of removal during precipitation, but also on how often precipitation occurs. It may be useful to consider this important point in some detail. Following Rodhe and Grandell (1972, 1981), we assume a constant scavenging coefficient λ_p to apply during precipitation. If we think of the sequence of dry and wet periods experienced by a pollutant-carrying particle or trajectory, the rate of wet removal that applies may be taken as a stochastic process (t) defined by

$$\lambda(t) = \begin{cases} 0 \text{ if dry period at t} \\ \lambda_p \text{ if precipitation occurs at t} \end{cases} \tag{5}$$

Assuming now that $\lambda(t)$ is a Markov process with stationary transition probabilities, the lengths of the dry and wet periods are exponentially distributed. If τ_d and τ_p are the average lengths of dry and wet periods experienced by the moving particle, it can be shown that the average residence time T_p for the pollutant with respect to wet deposition is

$$T_p = \tau dP_d + \frac{\tau_d + \tau_p}{\tau_d} \frac{1}{\lambda_p} \tag{6}$$

where P_d is the probability of a dry period at the starting point of the moving particle. Given the transport winds then T_p, together with the corresponding residence time T_d for dry deposition, determine the deposition of pollutant as a function of travel distance.

Relationships similar to (6) may be derived with slightly other assumptions (see Rodhe and Grandell (1981)). The quantities τ_d and τ_p have been estimated by Hamrud et al. (1981) from trajectories and precipitation data. τ_d was found to be 51 hours in summer and 53 hours in winter, whereas τ_p was 11 hours in both cases. If we take $\tau_d = 50$ hours, $\tau_p = 10$ hours, $\lambda_p^{-1} = 1$ hour and approximate the Eulerian probability from the Lagrangian data, i.e.

$$P_d = 1 - \frac{\tau_p}{\tau_d + \tau_p} = 0.83$$

then (6) yields

$$T_p = 50 \text{ hours} \times 0.83 + 6 \times 1 \text{ hour} = 47.5 \text{ hours}$$

This shows that for pollutants that are relatively efficiently removed during rain, such as sulphur, the average length of a dry period is key quantity for the determination of T_p, and hence for the wet deposition pattern. T_p is less sensitive to λ_p: if λ_p is changed by a factor of two in either direction, T_p varies between 44.5 and 53.5 hours.

It is therefore important that the precipitation data used by any model imply a correct value of T_p. This may be difficult to achieve, due to the time and space resolution of precipitation data available from the WMO station network. Precipitation amounts are generally measured in periods of 12 or 6 hours. In Europe the spacing of the stations available on the WMO telecommunication network is such that a 150 km grid element over land will contain two to three reporting stations on the average. If the calculations are based on gridded precipitation amounts, these are averaged out in time and space, with overestimated duration and under-estimated intensity. For a trajectory moving through such a precipitation field, τ_d will be too short, perhaps leading to an incorrect value for T_p.

THE SENSITIVITY OF CONCENTRATIONS OF SULPHUR DIOXIDE AND PARTICULATE SULPHATE, AND OF TOTAL SULPHATE DEPOSITION, TO CHANGES IN THE CHEMICAL TRANSFORMATION RATE

A. Basic Equations

To investigate this question one can also use the simple long-term dispersion model of Rodhe (1972), but changed to include the transformation of sulphur dioxide to sulphate, following Venkatram (1983). Like the Rodhe model, this model describes the spread of sulphur from a point source of strength Q over an angle θ, within a mixed layer of constant height h. If C_1 and C_2 are the concentrations of sulphur dioxide and sulphate respectively, it is convenient to define the fluxes

$$\left.\begin{aligned} G &= C_1\,u\theta rh \\ S &= C_2\,u\theta rh \end{aligned}\right\} \qquad (7)$$

where u is an average velocity and r is the distance from the source. The fluxes G and S change with travel time t due to deposition, described by average rates λ and $\bar{\lambda}$, and to transformation with an average rate k_t. The resulting mass-balance equations are

$$\left.\begin{aligned} \frac{dG}{dt} &= -\lambda G - k_t G \\ \frac{dS}{dt} &= -\bar{\lambda} S + k_t G \end{aligned}\right\} \qquad (8)$$

where sulphur dioxide and sulphate both are measured in sulphur units.

These first-order equations with constant coefficients can be easily solved for G and S. Transforming back to C_1 and C_2 using (3.1), and substituting r/u for t, one obtains

$$C_1 = \frac{(1-\beta)Q}{u\theta rh} \exp\,[-(\lambda + k_t)\,\frac{r}{u} \qquad (9)$$

$$C_2 = \frac{k_t}{\alpha} \cdot \frac{(1 - \beta)Q}{ur\theta h} \cdot \exp\,(-\bar{\lambda}\,\frac{r}{u}) \cdot [1 - \exp\,(-\,\alpha\,\frac{r}{u})] + \frac{\beta Q}{u\ rh} \cdot \exp\,[-\bar{\lambda}\,\frac{r}{u}] \qquad (10)$$

where

$$\alpha = \lambda - \bar{\lambda} + k_t \qquad (11)$$

To parameterize a faster transformation to sulphate just after emission, we have assumed that a small part β of the sulphur is emitted directly as particulate sulphate. $\beta = 0.05$ gives reasonable agreement between observed and calculated particulate sulphate concentrations (see EMEP/MSC-W Report 1/82 and earlier reports).

Differentiation of (9) and (10) with respect to the transformation rate k_t gives

$$\frac{dC_1}{C_1} = -t\ dk_t \qquad (12)$$

and

$$\frac{dC_2}{C_2} = \frac{\alpha^{-1}[\alpha - k_t - (\alpha - k_t\ (1 + t\alpha))\ \exp\,(-t\alpha)]}{k_t\ (1 - \exp\,(-t\alpha))}\ dk_t \qquad (13)$$

where

$$t = \frac{r}{u} \qquad (14)$$

The equations (12) and (13) determine the sensitivity of the concentrations C_1 and C_2 with respect to small variations in k_t. C_1 and C_2 depend linearly on the initial sulphate emission parameter β.

The deposition D of sulphur (mass per unit area and time) is related to the change in the flux of total sulphur:

$$\frac{d}{dr}\ (G + S) = -\ \theta r D \tag{15}$$

Addition of the two equations (8) gives

$$u\ \frac{d}{dr}\ (G + S) = -\ \lambda G - \bar{\lambda} S \tag{16}$$

Elimination of $\frac{d}{dr}$ $(G + S)$ from (15) and (16), and use of (7) gives a relationship between the deposition D and the concentrations:

$$D = h\ (\lambda C_1 + \bar{\lambda} C_2) \tag{17}$$

B. Parameter Values

We now choose parameter values that are thought to be appropriate for a summer situation:

τ_d	Average Lagrangian dry period	50 hours
τ_p	Average Lagrangian wet period	10 hours
P_d	Eulerian probability for dry period	0.83
λ_p^{-1}	Rate of wet removal during precipitation	$(1\ \mathrm{hr})^{-1}$
v_d	Deposition velocity for sulphur dioxide	$0.8\ \mathrm{cms}^{-1}$
w_d	Deposition velocity for particulate sulphate	$0.2\ \mathrm{cms}^{-1}$
h	mixing height	1200 m
k_t	Transformation rate	$8 \cdot 10^{-6}\ \mathrm{s}^{-1}$
β	Initial sulphate emission	0.05
u	Average windspeed	$10\ \mathrm{ms}^{-1}$

These choices imply the following values:

λ	Average removal rate for sulphur dioxide	$1.25 \cdot 10^{-5}\ \mathrm{s}^{-1}$
$\bar{\lambda}$	Average removal rate for particulate sulphate	$7.5 \cdot 10^{-6}\ \mathrm{s}^{-1}$
$\alpha = \lambda \quad \bar{\lambda} + k_t$		$1.3 \cdot 10^{-5}\ \mathrm{s}^{-1}$

C. Results

Figure 3 shows the concentration C_1 of sulphur dioxide as a function of the distance r from the source, when the constants are chosen according to the table above. The curve for C_1 is given in dimensionless units relative to the concentration $C_o = (1-\beta)Q/u\theta h \cdot 10$ km, which would be the value of C_1 at $r = 10$ km if sulphur dioxide were not removed or transformed. Figure 4 shows the concentration C_2 of particulate sulphate, also scaled against C_o. The ratio C_2/C_1 is given as a broken line in Figure 3. Close to the source, C_2 is considerably smaller than C_1, but since sulphate is slower removed, C_2 decreases slower with increasing r and overtakes C_1 at $r \approx 750$ km ($C_1/C_2 = C_2/C_o \approx 3.8 \cdot 10^{-3}$).

We now want to investigate the sensitivity of C_1, C_2 and D with respect to changes in the continuous transformation rate k_t and the initial sulphate emission parameter β. We choose to vary k_t by $\Delta k_t = 10^{-6}\ s^{-1}$ or by 12.5%. We vary β by $\Delta\beta = 0.05$ or by 100%.

Figure 5 shows the relative changes $\Delta C_1/C_1$ and $\Delta C_2/C_2$ resulting from an increase of k_t by Δk_t. We see that $\Delta C_1/C_1$ is small and negative close to the source, but increases swiftly in magnitude outside $r = 100$ km. At the same time, however, C_1 decreases in importance compared to C_2. The relative change $\Delta C_2/C_2$ is always positive, with a maximum of about 8.5% at $r \approx$ 400 km. The relative change in the total sulphur deposition $\Delta_k D/D$ is small and negative close to the source, since it is then determined mainly by $\Delta C_1/C_1$. Further away from the source, C_2 becomes larger than C_1, so $\Delta_k D/D$ is then determined more by $\Delta C_2/C_2$. It then changes sign and becomes positive. Obviously, $\Delta_k D/D \rightarrow \Delta C_2/C_2$ as $r \rightarrow \infty$. At all distances of interest, the negative ΔC_1 and the positive ΔC_2 partly compensate each other, so that $|\Delta_k D/D| < 5\%$.

Finally, the broken line in Figure 3.3 shows the relative change $\Delta D_\beta/D$ which results if $\beta = 0.00$ is assumed instead of $\beta = 0.05$. This implies that no initial very swift oxidation to sulphate is assumed. Close to the source, D will therefore be increased, due to the increase produced in C_1.

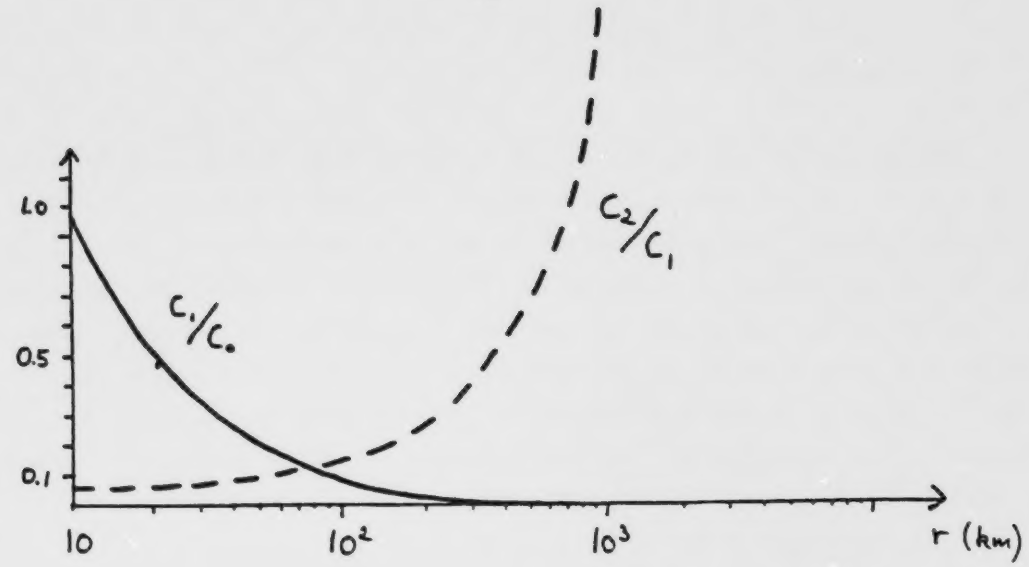

Figure 3. Calculated concentration C_1 of sulphur dioxide as a function of distance r from the source according to equation (3.3), constants given in Table 3.1. The curve for C_1 (solid line) is given in dimensionless units relative to the concentration $C_0 = (1 - \beta)Q/u\theta h \cdot 10$ km. Also shown, as a broken line, is the ratio C_2/C_1 between the concentrations of particulate sulphate and sulphur dioxide.

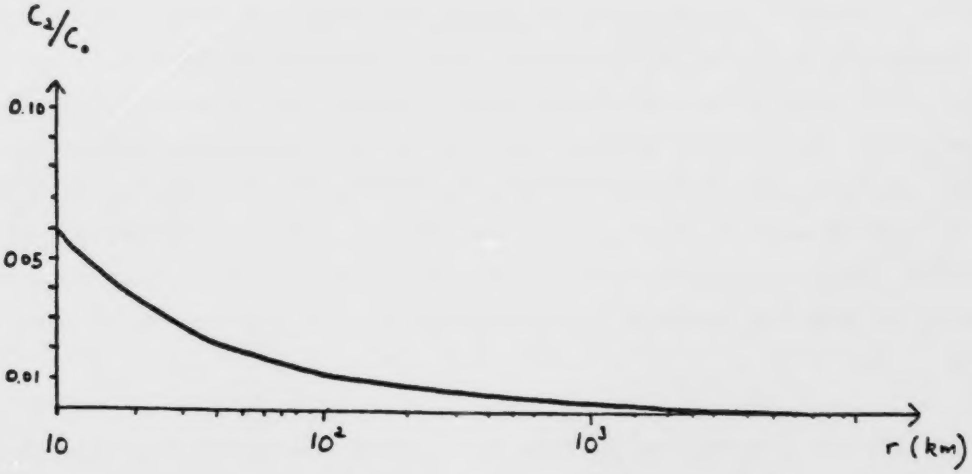

Figure 4. Calculated concentration C_2 of particulate sulphate as a function of distance r from the source, scaled against $C_0 = (1 - \beta)Q/u\theta h \cdot 10$ km.

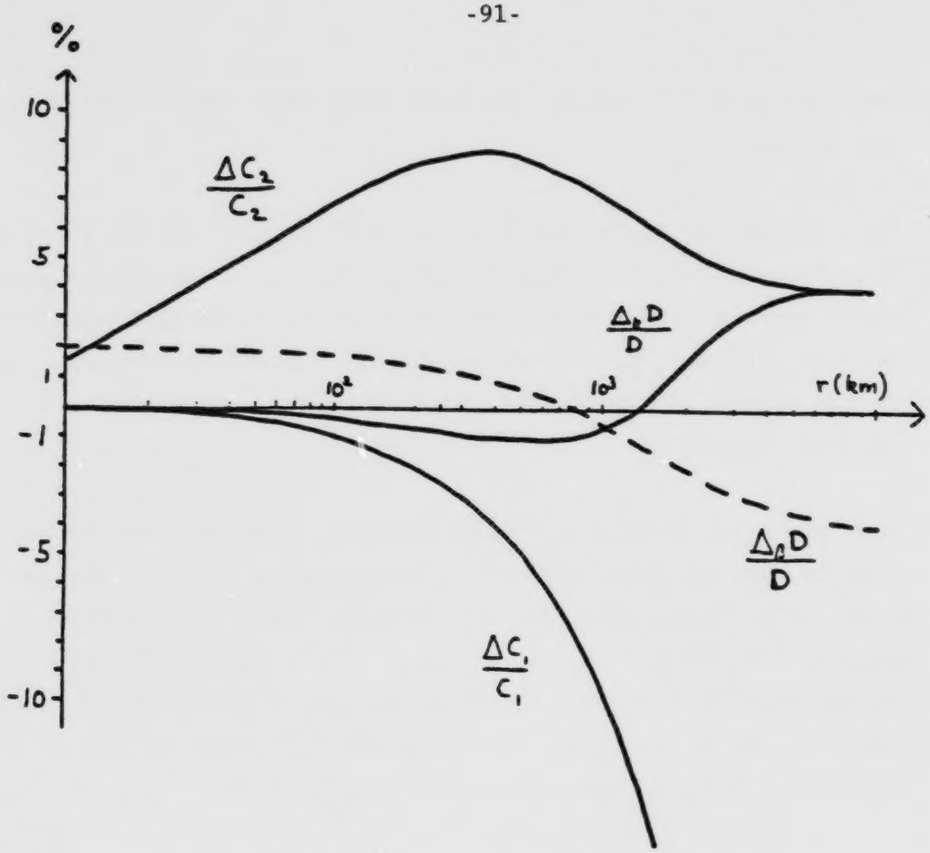

Figure 5. Relative changes $\Delta C_1/C_1$ and $\Delta C_2/C_2$ resulting from an increase of k_t from $8\cdot 10^{-6}\ s^{-1}$. The implied relative change $\Delta_k D/D$ in the total sulphur deposition is also shown. Finally, the relative change $\Delta_\beta D/D$ in the total sulphur deposition implied by changing the initial sulphate emission parameter β from 0.05 to 0.0 is shown as a broken line.

Far away, D decreases, since C_2 decreases. At all distances of interest, $|\Delta D_\beta/D| < 5\%$.

D. Conclusions

a) The sensitivity of the sulphur dioxide concentrations to variations in the transformation rate is small close to the source (closer than a few hundred km). Further away, sensitivity is large. However, concentrations of sulphur dioxide become unimportant compared to sulphate concentrations from about 7-800 km from the source.

b) The sensitivity of the particulate sulphate concentration to the transformation rate (taken as both a very swift local rate just after emission and a slow large-scale rate) is large close to the source. However, the concentration of particulate sulphate close to the source is unimportant compared to the concentration of sulphur dioxide.

Far away from the source, (more than say, 1000 km), the sensitivity is smaller since there is time enough to produce sulphate even if the transformation rate is slow. In an intermediate range, (300-800 km from the source) a 10% change in the transformation rate will produce a similar change in the sulphate concentration, and at the same time the sulphate concentration and the sulphur dioxide concentration will be comparable.

c) Total deposition close to the source is determined mainly by dry deposition of sulphur dioxide. The sensitivity to the transformation rate is small because of a) above.

Far away from the source, the total deposition is determined mainly by wet deposition of particulate sulphate. Sensitivity to the transformation rate is only moderate because of the last part of b) above.

In the intermediate range, sensitivity is small because of counteracting effects: An increase in the transformation rate will reduce the deposition of sulphur dioxide, but at the same time increase the deposition of particulate sulphate.

A SUMMARY OF THE SITUATION FOR LAGRANGIAN MODELS

This summary is based mostly on the material in the preceding chapters. Some new points are, however, also introduced.

The uncertainty of a diagnostic trajectory position, measured by the standard deviation between trajectory and tetroon positions, is roughly five times larger than the standard deviation of an instantaneous plume. This means that one cannot expect to be able to calculate the instantaneous pollutant distribution at the plume resolution level.

For sampling times of one day or more, the individual plumes are smoothed out sufficiently by the synoptic weather systems, so that a reasonable agreement between calculated and measured first-order pollutant concentration is to be expected. Longer-term (monthly, annual) concentration patterns depend mainly on trajectory path statistics and emission distribution, the uncertainty of individual trajectories being unimportant.

A constant error in the deposition velocity will produce a relative error in the concentration of a primary pollutant that increases linearly with travel time. On the regional scale, the dry deposition pattern is only moderately sensitive to the deposition velocity.

For pollutants that are removed relatively fast during precipitation, the long-term wet deposition pattern will depend on the Lagrangian dry time as well as on trajectory path statistics and the emission distribution. It is not very important to know exactly how fast the pollutant is removed during rain, as long as the removal rate is reasonably fast (time scale up to a few hours, say).

Total (wet + dry) deposition of sulphur close to the source is determined mainly by the dry deposition of sulphur dioxide. Sensitivity to changes in the transformation rate from sulphur dioxide to sulphate is small. Far away from the source, the total deposition is determined mainly by the wet deposition of particulate sulphate. Sensitivity to the transformation rate is moderate. In the intermediate range, sensitivity is small because of counter-acting effects: An increase in the transformation rate will reduce the deposition of sulphur dioxide, but at the same time increase the deposition of particulate sulphate.

In general, the sensitivity of the total long-term sulphur deposition pattern to the main determining physical parameters is not particularly great.

Complex non-linear chemical schemes are difficult to handle in Lagrangian models. In source-oriented models, where "puffs" emitted from different sources are followed separately, difficulties arise when puffs emitted from different sources overlap. If the chemical species in the overlapping puffs are allowed to interact, the subsequent redistribution back into the individual puffs is indeterminate because of the nonlinearity. Similar problems arise in receptor-oriented models if horizontal diffusion is specifically included, in this case different "puffs" will also overlap. If emission and other model input are given on a relatively coarse (∿ 150 km) spatial scale, however, specific inclusion of horizontal diffusion is not necessary. In this simple case we have a "moving box" model, where non-linear chemistry can be easily included.

In principle, however, any model that includes non-linear chemistry should have its emissions given on a finer spatial, to avoid errors due to spatial overaging. Calculations with a finer spatial scale are only meaningful, however, if the fine-scale accuracy can be preserved in the transport calculations. At present, the uncertainties in the trajectory calculations are too large for this to be possible.

Calculations with high-spatial resolution models are thus only to be taken as one realization of a stochastic process, that approximates closely a possible occurrence in nature. In other words, such calculations will demonstrate possibilities of what actually can happen, but will not necessarily be very similar to what actually did happen during the episode under investigation. If such calculations are to be used to suggest some form of optimum emission reduction strategy, a considerable number of such calculations are needed, that together comprise a relevant climatological average. Because of the non-linear effects, the model will have to be re-run on the same meteorological data for every emission scenario. Such a procedure is rather resource-demanding.

REFERENCES

Carras, J.N. and D.J. Williams (1981). The Long Range Dispersion of a Plume from an Isolated Point Source. **Atmos. Environ.**, **15**:2205-2217.

Clark, P.A., B.E.A. Fisher and A.R.W. Marsh (1983). A Case Study of Sulphur Oxides and Other Acid Rain Precursors Out to 650 km From Industrial Areas of the United Kingdom. CEGB Report TPRD/L/2325/N82.

Clarke, J.F., T.L. Clark, J.K.S. Ching, P.L. Haagenson, R.B. Husar and D.E. Patterson (1983). Assessment of Model Simulation of Long-Distance Transport. **Atmos. Environ.**, **17**:2449-2462.

Gifford, F.A. (1982). Horizontal Diffusion in the Atmosphere: A Lagrangian-Dynamical Theory. **Atmos. Environ.**, **16**:505-512.

Hamrud, M., H. Rodhe and J. Grandell (1981). A Numerical Comparison Between Lagrangian and Eulerian Rainfall Statistics. **Tellus**, **33**:235-241.

Hefter, J.L. (1980). Air Resources Laboratories Atmospheric Transport and Dispersion Model. NOAA Tech. Memo. ERL ARL-81, 24 pp.

Organization for Econimic Cooperation and Development (1977). The OECD Programme on Long Range Transport of Air Pollutants. Measurements and Findings. OECD, Paris.

Rodhe, H. (1972). A Study of the Sulphur Budget for the Atmosphere Over Northern Europe. **Tellus**, **24**:128-138.

Rodhe, H. and J. Grandell (1972). On the Removal Time of Aerosol Particles from the Atmosphere by Precipitation Scavenging. **Tellus**, **24**:442-454.

Rodhe, H. and J. Grandell (1981). Estimates of Characteristics Times for Precipitations Scavenging. **J. Atmos. Sci.**, **38**:370-386.

Smith, F.B. (1979). The Character and Importance of Plume Lateral Spread Affecting the Concentration Downwind of Isolated Sources of Hazardous Airborne Material. WMO Symposium on the Long Range Transport of Pollutants and Its Relation to General Circulation Including Stratospheric/ Tropospheric Exchange Processes. Sofia, 1-5 October 1979. WMO No. 538, 241-251.

Taylor, A.D. (1982). Puff Growth in an Ekman Layer. **J. Atmos. Sci.**, 39: 837-850.

Venkatram, A. (1983). Air Quality Over Long Distances. To be published in **Handbook of Applied Meteorology**.

CHAPTER IV

STOCHASTIC LONG RANGE TRANSPORT MODELS

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INTRODUCTION

A long range transport model is characterized as stochastic when it is based upon models for the probabilities of selected events associated with long range transport and deposition. Most stochastic models are designed to estimate long-term values of concentration and deposition of pollutants through equations of the type:

$$C(\tilde{x}_r) = \sum_s Q(\tilde{x}_s) \int_0^\infty p(\tilde{x}_r|\tilde{x}_s;\, t)\, dt \tag{1}$$

In (1), $C(\tilde{x}_r)$, the concentration at a receptor $\tilde{x}_r$, is taken to be the sum of contributions from sources $Q(\tilde{x}_s)$ located at $\tilde{x}_s$, and $p(\tilde{x}_r|\tilde{x}_s;\, t)$ is the probability that a particle released at $\tilde{x}_s$ is found at $\tilde{x}_r$ in travel time t from release. A similar equation can be written for the deposition of the pollutant at $\tilde{x}_r$.

The function $\int_0^\infty p(\tilde{x}_r|\tilde{x}_s;\, t)\, dt$ can be estimated by sampling over a large number of simulations of the evolution of a pollutant "particle" as it travels from $\tilde{x}_s$ to $\tilde{x}_r$. This is the basis of the Monte-Carlo technique used by Patterson et al. (1980) and Shannon (1981) to model long range transport of sulfur. We will not examine this type of model in this paper. Our discussion will be confined to long range transport models that estimate $p(\tilde{x}_r|\tilde{x}_s;\, t)$ through heuristic probability models. In most cases, such models assume the following decomposition,

$$p(\tilde{x}_r|\tilde{x}_s;\, t) = M(\tilde{x}_r|\tilde{x}_s;\, t)\cdot D\,(\tilde{x}_r|\tilde{x}_s;\, t) \tag{2}$$

Here, M( ) depends only upon removal processes such as dry deposition and wet scavenging, and D( ) is a function of large scale dispersion in the absence of scavenging. The following sections describe models for M( ) and D( ). It should be noted that stochastic LRT models are empirical in the sense that it is not possible to provide rigorous justification for all the assumptions on which they are based. Their validity derives primarily from the goodness of fit between model estimates and corresponding observations.

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THE SCAVENGING PROBABILITY M

Most models for $M(\tilde{x}_r|\tilde{x}_s;\ t)$ are based on equations first derived by Rodhe and Grandell (1972). Therefore, it is useful to examine these equations in some detail here. Our derivation is less rigorous than that of Rodhe and Grandell. However, our heuristic approach provides a better "fell" for the physics governing the stochastic equations. The scavenging model assumes that the pollutant in the atmosphere can exist in one of two states, namely the dry state (d) and the wet state (w). A particle is said to be in the wet state when it is embedded within a synoptic scale rain system. By distinguishing between these two states we account for the profound influence of clouds and precipitation on the chemistry and scavenging of pollutants.

To derive the equations governing the evolution of these two states we define the following probabilities,

$p_d(t)$ = probability that a particle is in the dry state after travel time t

$p_w(t)$ = probability that a particle is in the wet state after travel time t

Figure 1 shows the interaction between the two states. We see that a particle can undergo a transition from one state to another. For example, when a particle leaves a rain system it enters the dry state. The transition rates between the two states are denoted by μ_{wd} and μ_{dw}. We also allow for removal of particles from the two states. These removal rates are signified by λ_d and λ_w. The diagram allows us to write down the differential equations for p_d and p_w.

$$\frac{dp_d}{dt} = -\lambda_d p_d - \mu_{dw} p_d + \mu_{wd} p_w \tag{3a}$$

$$\frac{dp_w}{dt} = -\lambda_w p_w - \mu_{wd} p_w + \mu_{dw} p_d \tag{3b}$$

We will assume that the transition rates do not depend upon the past history of the particles. In technical terms, this process controlling the evolution of the pollutant particles is said to be a Markov process.

Before we extend Eqs. (3a) and (3b) to make them applicable to sulfur deposition, we will discuss the estimation of the parameters in the equations.

A. Parameter Values

The rates at which the pollutant switches from the dry state to the wet state and vice versa is determined by the average length of time the pollutant spends in each of these states. Because the definition of these states is somewhat arbitrary, the determination of the average periods τ_d and τ_w is uncertain. Rodhe and Grandell (1972) have estimated these parameters from fixed point (Eulerian) statistics of precipitation. By assuming that it was dry whenever the precipitation rate was less than 0.25 mm hr^{-1} they found that $\tau_d = 68$ hrs and $\tau_w = 7$ hrs for the year 1966 at a weather station near Stockholm, Sweden. There is no reason to expect the average motion of precipitation systems past a fixed observer to be different from that past an observer following pollutants in the boundary layer. This expectation is borne out by a recent study conducted by Hamrud and Rodhe (1981) who showed that there is little difference between Eulerian and Lagrangian statistics. Therefore, estimates of τ_d and τ_w from fixed stations provide guidance on appropriate values for the scavenging model.

Henmi and Reiter (1978) have calculated τ_d and τ_w from rainfall data collected at 61 stations distributed over the Eastern United States. Their estimates of τ_d for 1974 range from 60-75 hours, and those of τ_w from 2-5 hours. Slinn et al. (1979) have based their estimates of these time scales on trajectories originating from Kansas City. They found that average values derived from calculations for January and July 1975 were $\tau_d = 46$ h and $\tau_w = 7$ h. Our survey of the literature indicates that $\tau_d = 100$ h and $\tau_w = 10$ h are acceptable values for modeling the scavenging of sulfur.

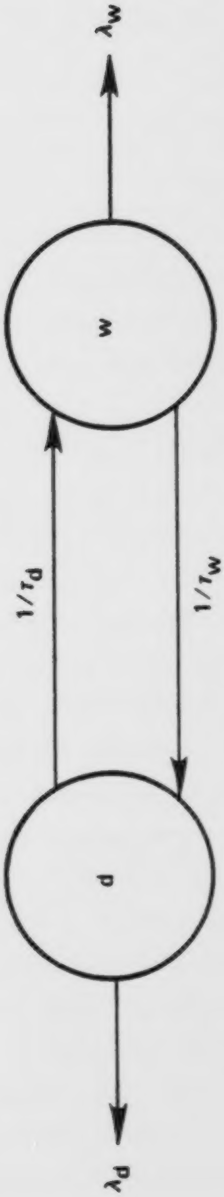
λ_w
w
$1/\tau_d$
$1/\tau_w$
d
λ_d

Figure 1. State representation for the scavenging model.

Now how are these estimates of τ_d and τ_w related to μ_{wd} and μ_{dw}? Observations (Rodhe and Grandell, 1972) indicate that the lengths of wet and dry periods are exponentially distributed. That is, the probability that the duration of a wet period exceeds t is given by

$$p(\tau > t) = e^{-t/\tau_w} \tag{4}$$

In defining a wet interval we consider only those periods which start off wet and remain wet during the period; we do not allow dry periods to switch to wet periods. If introduce this condition into Eq. (3b) and set $\lambda_w = 0$, we find that

$$p_w(t) = e^{-\mu_{wd}t}; \; p_w(0) = 1 \tag{5}$$

We immediately see that

$$\mu_{wd} = 1/\tau_w \tag{6a}$$

Similarly,

$$\mu_{dw} = 1/\tau_d \tag{6b}$$

We can readily understand these equations from an intuitive viewpoint. If the average length of wet periods is small, particles in wet periods enter dry periods rapidly; the rate at which particles enter a dry state from a wet state should increase as τ_w decreases. This is what Eq. (6a) says.

The dry scavenging rate λ_d is related to the dry deposition velocity v_d of the pollutant through the equation

$$\lambda_d = v_d/h \tag{7}$$

Here h is the effective height through which the pollutant diffuses before being dry deposited at the ground. In principle, h can be modified to account for vertical structure of the concentration field. This means that λ_d has to vary with travel time t, and the stochastic differential equations have to be solved numerically. Experience (Venkatram et al. 1982) indicates that there is little to be gained by using a time varying λ_d except very close to a source. For annual average estimates of deposition, one usually takes h to be a constant whose magnitude is identified with that of the mixed layer height z_i.

Although the dry deposition velocity v_d is known to vary with space and time, empirical evidence shows that taking $v_d = 1$ cms^{-1} for SO_2 and $v_d = 0.1$ cms^{-1} for SO_4 provides acceptable estimates of concentration and deposition (Fisher and Clark, 1983).

The wet removal rate λ_w is in general a complicated function of cloud physics, and aqueous phase chemistry of the pollutant. Our experience with stochastic modeling indicates that a constant value of $\lambda_w \simeq 10^{-4}$ s^{-1} for both SO_2 and SO_4 (Fisher and Clark, 1984; Venkatram et al., 1982) yields acceptable estimates of sulfur wet deposition.

A parameter that will appear in the subsequent discussion is the SO_2 to SO_4 conversion rate which we denote by k. We know that the transformation of SO_2 to SO_4 is controlled by the concentration of the OH radical which in turn depends upon complex photochemistry. Measurements and theory (See Calvert et al., 1984) show that although k can vary by a factor of 10, a good "average" value is 1% h^{-1}.

It is necessary to point out again that the stochastic LRT model is an empirical model. The correctness of the values used in the model is established primarily by the goodness of fit between model predictions and observations. However, the credibility of such a model is enhanced if we can show that the parameter values are consistent with our knowledge of the processes they represent. This is what we have done in the preceding paragraphs. Note that it is not meaningful to criticize the use of constant values for these parameters because there is no a priori reason for allowing them to vary with space and time. We would, of course, make these parameters vary if the modification resulted in a better fit between model predictions and observations. This is the principle that guides improvements in empirical models. The next section describes how we can extend the concepts developed so far to the modeling of sulfur scavenging.

B. The Four State System - Sulfur

To allow for different SO_2 to SO_4 conversion rates during wet and dry states, Smith (1981) and Venkatram et al. (1982) made a modification to the two state system described earlier. The basic idea was to define four states instead of two. The states and associated probabilities are defined below,

$G_d(t)$ = probability that sulfur exists as SO_2(S(IV)) in the dry state at time t,

$G_w(t)$ = probability that sulfur exists as SO_2 in the wet state at time t,

$S_d(t)$ = probability that sulfur exists as SO_4(S(VI)) in the dry state at time t,

$S_w(t)$ = probability that sulfur exists as SO_4 in the wet state at time t.

Figure 2 shows the interaction diagram for this four state system. We can now write down the differential equations for this system.

$$\frac{dG_d}{dt} = -\lambda_d G_d - \frac{1}{\tau_d} G_d - k_d G_d + \frac{1}{\tau_w} G_w \tag{8a}$$

$$\frac{dG_w}{dt} = -\lambda_w G_d - \frac{1}{\tau_w} G_w - k_w G_w + \frac{1}{\tau_d} G_d \tag{8b}$$

$$\frac{dS_d}{dt} = k_d G_d - \bar{\lambda}_d S_d - \frac{1}{\tau_d} S_d + \frac{1}{\tau_w} S_w \tag{8c}$$

$$\frac{dS_w}{dt} = k_w G_w - \bar{\lambda}_w S_w - \frac{1}{\tau_w} S_d + \frac{1}{\tau_d} S_d \tag{8d}$$

These equations can be readily solved if we assume that the parameters λ and k are independent of G and S. Can we justify this assumption? It is well accepted (See Acid Deposition, 1983) that the concentration of the OH radical controls the gas phase oxidation of SO_2 to SO_4. A recent study (Stockwell and Calvert, 1983) shows that because the OH-SO_2 reaction is not

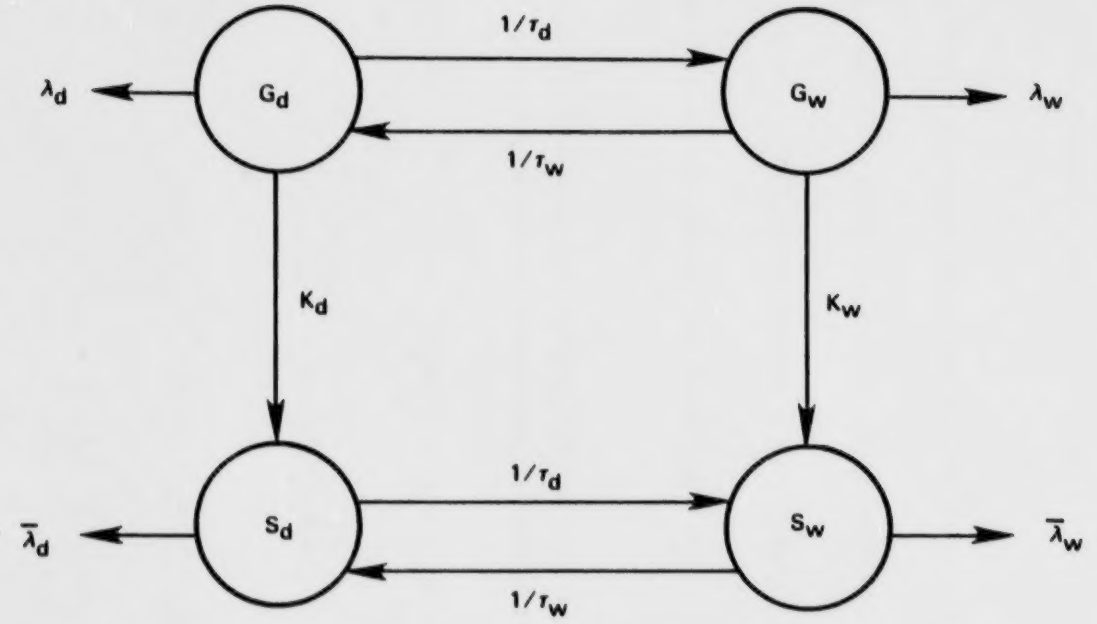
λ_d
G_d
$1/\tau_d$
$1/\tau_w$
G_w
λ_w
K_d
K_w
$\bar{\lambda}_d$
S_d
$1/\tau_d$
$1/\tau_w$
S_w
$\bar{\lambda}_w$

Figure 2. Probability interaction diagram for sulfur scavenging.

a chain terminating step in a NO rich atmosphere, the OH concentration is insensitive to the SO_2 concentration. Therefore, there is justification in taking k to be independent of G in using the model for Eastern North America (ENA).

Current research (See Hicks, Critical Assessment Document, USEPA) provides no reason to believe that the dry removal rates are sensitive to the concentrations of SO_2 and SO_4. The only parameter that is probably a function of the SO_2 concentration is the wet removal rate λ_w. However, current experience with stochastic modeling (Fisher and Clark, 1984; Smith, 1981) indicates that wet deposition fields of sulfur for 1980 can be reasonably described by $\lambda_w = 10^{-4}\ s^{-1}$. It is significant that this value is applicable to both the United States and Europe (Fisher and Clark, 1983).

In a recent paper, Venkatram and Pleim (1984) show how one can get around the assumption that λ_w is not a function of G. The trick is to use the observation that for the present mix of pollutants found over Eastern North America and Europe, SO_2 is removed very efficiently in rain events. This is equivalent to the statement $\lambda_w\tau_w >> 1$. This condition is certainly true if one accepts the empirically determined values $\lambda_w = 10^{-4}\ s^{-1}$ and $\tau_w = 10$ h given in the literature (Fisher and Clark, 1983; Smith 1981). We can make a similar statement about the wet removal of SO_4.

Then it is easy to see that the "destruction" terms in Eqs. (8b) and (8d) are dominated by wet removal. Because the time scales of production of G_w and S_w, τ_d is much larger than the removal time scales ($\lambda_w\tau_d >> 1$) we can assume that G_w and S_w are governed by quasi-steady equations.

$$G_w = \frac{1}{\lambda_w\tau_d} G_d \tag{9a}$$

$$S_w = \frac{1}{\lambda_w\tau_d} S_d \tag{9b}$$

We see immediately that the "wet" terms in Eqs. (8a) and (8d) can be neglected and we find that G_d and S_d are governed by the simple equations

$$\frac{dG_d}{dt} = -\left(\lambda_d + \frac{1}{\tau_d} + k_d\right) G_d \tag{10a}$$

and

$$\frac{dS_d}{dt} = -\ (\bar{\lambda}_d + \frac{1}{\tau_d})\ S_d + k_d G_d \tag{10b}$$

Notice that we are now left with a set of equations in which the parameters are essentially independent of G and S. Because there is no a priori reason to allow the parameters to vary with time, we will integrate the equation taking them to be constants

$$G_d(t) = G_d\ (0)\ \exp\ (-\ell_g t) \tag{11a}$$

and

$$S_d(t) = S_d(0)\ e^{-\ell_s t} + \frac{k_d G_d(0)}{(\ell_g - \ell_s)}\ (e^{-\ell_s t} - e^{-\ell_g t}) \tag{11b}$$

where the loss terms ℓ_s and ℓ_g are defined by

$$\ell_g = \lambda_d + \frac{1}{\tau_d} + k_d \tag{12a}$$

$$\ell_s = \bar{\lambda}_d + \frac{1}{\tau_d} \tag{12b}$$

The preceding equations have to be combined with an appropriate dispersion probability to yield a stochastic LRT model. The next section reviews current formulations of the dispersion probabilities.

THE DISPERSION PROBABILITY

It is customary to write the dispersion probability $D(\tilde{x}_r | \tilde{x}_s;\ t)$ as follows:

$$D(\tilde{x}_r | \tilde{x}_s;\ t) = V \cdot H \tag{13}$$

Here V is a function of vertical dispersion and H that of horizontal dispersion. Fisher (1978) identifies V with the solution of the one-dimensional diffusion equation

$$\frac{dC}{dt} = \frac{\partial}{\partial z} (K \frac{\partial C}{\partial z}) \qquad (14)$$

with the boundary and initial conditions given by

$$\frac{\partial C}{\partial z} = 0; \; z = z_i \qquad (15a)$$

$$K \frac{\partial C}{\partial z} = v_d C; \; z = z_r \qquad (15b)$$

and

$$C \; (z,0) = Q\delta \; (z - h_s) \qquad (16)$$

where z_i is the mixed layer height, z_r is a reference height, Q is the instantaneous source strength, h_s is the effective stack height and δ is the Dirac delta function. Fisher derives an analytical solution for a constant eddy diffusivity K, and extends the solution to a continuous point source using the transformation,

$$t = r/uf_\theta \qquad (17)$$

In (17), r is the distance between $\tilde{x}_r$ and $\tilde{x}_s$, u is an average mixed layer wind and f_θ if the relative frequency with which the wind blows from $\tilde{x}_s$ to $\tilde{x}_r$. Note that if the likelihood of the wind blowing in any direction is the same, $f_\theta = 1$. Because the solution accounts for dry deposition, the stochastic scavenging model treats only wet removal in Fisher's study.

We can object to the use of the concept of eddy diffusivity in modeling vertical dispersion close to a source. However, it represents a reasonable empirical method to account for incomplete vertical mixing close to an elevated source of pollutants. By not considering the vertical structure of the concentration, we can overestimate dry deposition close to the source and thus underestimate the amount of material available for wet deposition far away from the source. This effect can be important during stable conditions when elevated plumes become decoupled from the ground, and can travel hundreds of miles without undergoing dry deposition. At the present time, there is no empirical evidence (Fisher, 1982) to indicate that assumptions about V(z,t) make much difference to the predicted deposition far away from a source. However, I think we are doing something wrong here, and correct modeling of vertical structure might explain the underestimation of wet deposition at remote areas in the U.S. and Europe (See Fisher and Clark, 1983).

The simplest horizontal dispersion function is based on the assumption that trajectories originating from a source, are almost straight over distances of the order of 1000 km. Then H(r,t) can be written as (Fisher, 1978).

$$H(r,t) = \frac{f_\theta}{2\pi r u} \tag{18}$$

An alternative H(r,t) is that given by the Gaussian puff equation

$$H(\tilde{x}_r|\tilde{x}_s;\ t) = \frac{1}{2\pi\alpha_x\alpha_y} \exp\left(-\frac{(x-\bar{x})^2}{2\alpha_x^2} - \frac{(y-\bar{y})^2}{2\alpha_y^2}\right) \tag{19}$$

The parameters of the distribution $\bar{x}(t)$, $\bar{y}(t)$ are the coordinates of the mean particle position after travel time t from release. The dispersion parameters $\sigma_x(t)$ and $\sigma_y(t)$ are the standard deviations of the particles positions about $\bar{x}$ and $\bar{y}$. The coordinates of the receptor $\tilde{x}_r$ are (x,y). Bolin and Persson (1975) have estimated these dispersion parameters using trajectory statistics over Europe. Venkatram et al. (1982) based their H(r,t) for North America on the assumption that in mid-latitudes the mean flow is zonal from the west to the east. Cyclones and anticyclones carried by this mean flow can be then looked upon as turbulent eddies whose velocity statistics determine σ_u and σ_v. Based on some work done by Tennekes (1977), the following tentative dispersion parameters were suggested,

$$\bar{x} = ut;\ \bar{y} = 0 \tag{20}$$

where

$$u = 10\ \mathrm{ms}^{-1},\ \alpha_u = 10\ \mathrm{ms}^{-1},\ \alpha_v = 6\ \mathrm{ms}^{-1} \tag{21}$$

Surprisingly, these estimates provided reasonable predictions of annually averaged wet sulfur deposition measured in 1977 at sites in Eastern North America (Venkatram et al., 1982).

It is useful to point out that the use of the Gaussian puff equation in the concentration equation (1) involves a convolution with the scavenging solutions. This procedure entails numerical integration which is inconvenient when a large number of sources is considered. On the other hand, Eq. (18) with the transformation (17) uncouples the scavenging from the dispersion probability which is an advantage from a computational viewpoint. As we will see later there is no compelling reason to use the more complicated dispersion probability.

APPLICATION OF STOCHASTIC LRT MODELS

Bolin and Persson (1975) were probably the first to use a stochastic LRT model to estimate sulfur deposition. They calculated the dispersion probability by sampling a large number of trajectories originating from selected points in Western Europe. Horizontal dispersion was formulated in terms of the Gaussian puff equation discussed earlier. Vertical dispersion corresponded to the numerical solution of the one dimensional diffusion equation.

The scavenging probability was estimated with the two state system described earlier. The long-term concentration was estimated by doing the calculation assuming that there was no rainfall, and then simply multiplying the result by either $p_w(t)$ or $p_d(t)$ to obtain the concentration during the appropriate state. Estimates from this model were in broad agreement with measurements of wet sulfur deposition over Europe.

Fisher (1975, 1978) followed a similar approach except that his horizontal dispersion probability was based on the trajectory weighting scheme of Eq. (18). Also, he used an analytical solution of the diffusion equation to represent the vertical dispersion probability. He assigned a value of f_θ to each of eight sectors he used. Vertical dispersion was based on five stability classes, each of which was associated with a frequency, wind speed, mixed layer depth and eddy diffusivity. Predictions of wet deposition of sulfur from the model were consistent with observations obtained from the OECD network.

Smith (1981) and Venkatram et al. (1982) based their LRT models on the four state sulfur system. This modification was motivated by the observation (Wilson and Gillani, 1979) that the SO_2 to SO_4 conversion rate was higher during humid (wet) conditions than during dry conditions. The four state system allows us to differentiate between the chemical processes of the two states. Venkatram et al. (1982) combined this scavenging model with the Gaussian puff horizontal dispersion probability to make estimates of wet deposition of sulfur over Eastern North America. The predicted pattern compared well with the observed pattern obtained during 1977 from Canadian and U.S. precipitation chemistry networks.

Studies performed by Fisher and Clark (1983) and Venkatram and Pleim (1983) showed that it was necessary to assume very efficient removal of SO_2 during wet conditions to explain observed patterns of wet sulfur deposition. This empirical result suggests efficient in-cloud conversion of SO_2 to SO_4. Under these conditions it is found that as long as λ_w is large, predictions are insensitive to k_w. Then there is little difference between the results of the two state and the four state system scavenging model. For a pollutant, such as NO_2, for which λ_w is not believed to be large, the four state system is a more realistic way to model scavenging and transformation processes.

There is ample evidence to indicate that stochastic LRT models can provide good descriptions of observed patterns of annually averaged wet deposition of sulfur. In a later section, we will provide quantitative measures of the degree of agreement between predictions and observations.

A. Application of the Model to Other Pollutants

For various reasons, the stochastic LRT model has been applied primarily to sulfur deposition. However, there are good reasons to believe that the model will be able to explain nitrate deposition. The primary route for the conversion of NO_2 to HNO_3 is through the OH radical whose concentration is not very sensitive to the concentrations of co-pollutants (Stockwell and Calvert, 1983). Although organic nitrates do contribute to the total nitrate concentration, there should be no serious objection to the use of a simple "linear" conversion rate k_d for the $NO_2 \rightarrow NO_3$ transformation. Because the OH concentration is likely to be small during wet (cloudy) conditions, k_w should be close to zero.

The solubility of NO_2 in water is low which suggests that we need not worry about the wet removal of NO_2, or the aqueous phase conversion of NO_2 to NO_3. The wet removal of nitrate itself is likely to be very efficient. The dry deposition velocity of NO_2 should be smaller than that of SO_2 while HNO_3 should be dry deposited rather efficiently. This sort of reasoning formed the basis for a modeling exercise performed by us for the Canadian Electrical Association (Lague, 1983). The parameters used in the LRT model were

$$v_d(NO_2) = 0; \; v_d(NO_3) = 1 \text{ cms}^{-1}$$

$$\lambda_w(NO_2) = 0; \; \lambda_w(NO_3) = 10^{-4} \text{ s}^{-1}$$

$$k_d = k_w = 10\% \text{ hr}^{-1}; \; z_i = 1000 \text{ m}$$

In hindsight it appears that we should have set $k_w = 0$. Model predictions for wet deposition of NO_3 were made at 34 stations at which measurements were available for 1980. The correlation (r^2) between model estimates and the observations distributed over North America had a surprisingly high value of 0.9. However, the model tended to under predict nitrate wet deposition by almost a factor of two. We believe that this discrepancy is related to the uncertainty in the NO_x emission inventory. The high r^2 is partly the result of using the observed rainfall to prorate the model estimates which were based on a constant annual rainfall amount of 0.88 m.

Fisher (1982) has also made estimates of wet nitrate deposition over Europe. Unlike us, he assumed that NO_2 was scavenged as efficiently as NO_3. His NO_2 to NO_3 conversion was 2% hr^{-1}. Figures 3 and 4 show that the model provides a reasonable description of the observed sulfate and nitrate profiles.

These preliminary attempts at estimating nitrate deposition are encouraging and suggest that, with further experimentation, we will be able to describe nitrate deposition as well as we have sulfate deposition. In the next section we will go into details of specific applications of the stochastic LRT model. This examination will provide quantitative measures of the performance of such models.

PERFORMANCE OF STOCHASTIC LRT MODELS

This section draws upon the experience we have had in estimating wet sulfur deposition with a stochastic model that combines the four state sulfur system with the trajectory rose dispersion model. We have assumed that $\lambda_w \tau_w >> 1$. This allows us to use the simple equations (11a) and (11b).

It is worthwhile to present the simple equation for wet deposition D_w that results from the combination of the scavenging and dispersion probabilities

$$D_w = \frac{Qf_\theta}{2\pi ru} \frac{1}{\tau_d} (G_d + S_d) \tag{22}$$

Notice that the length of the dry period τ_d controls the rate at which dry sulfur is supplied to the wet state where it is removed completely by wet scavenging. Equation (22) was used to estimate wet deposition of sulfur at the 62 stations listed in Table 1.

The emission inventory, compiled by ERT for the Canadian Electrical Association, is a composite of information from the EPA (Canada), NEDS and individual state inventories, and is nominally representative of 1980 (Lague, 1983). This inventory agrees well with that prepared by Working Group 3B under the U.S.-Canada Memorandum of Intent (MOI 1982). For use in

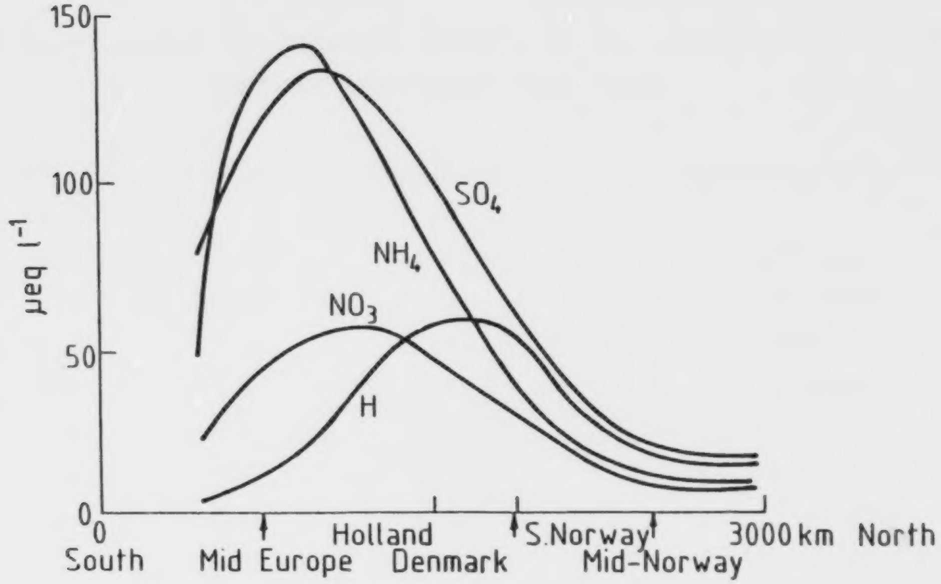

Figure 3. North-south profiles of ions in precipitation across Europe from EMEP and Dutch Networks (1978-9) (from Fisher, 1982).

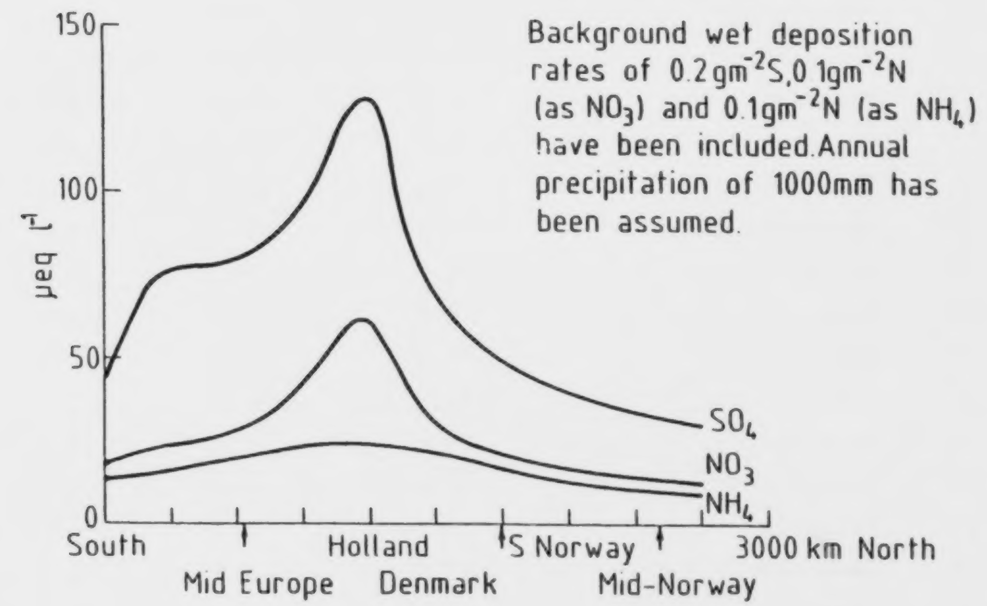

Figure 4. Calculated north-south profiles of ions in precipitation across Europe (from Fisher, 1982).

TABLE 1

COMPARISON OF OBSERVATIONS OF ANNUALLY AVERAGED WET DEPOSITION OF SULFUR WITH MODEL PREDICTIONS FOR 1980

No.	Station Name	Predicted	Observed	OBS/PRED
1	Long Point	14.1	11.6	0.8
2	Chalk River	7.2	8.2	1.1
3	Kejimkujek	4.5	6.0	1.3
4	Gander	1.1	7.1	6.6
5	Truro	3.3	8.9	2.7
6	St. John	8.3	11.7	1.4
7	Charlo	3.4	9.0	2.6
8	Sept-Iles	2.1	5.8	2.8
9	Goose	0.8	3.4	4.4
10	Fort Chimo	0.6	1.1	1.9
11	Nitchequon	1.4	2.6	1.9
12	Quebec	5.7	14.9	2.6
13	Chigougamau	3.3	5.1	1.6
14	St. Hubert	11.2	11.5	1.0
15	Maniwaki	6.4	10.1	1.6
16	Kingston	9.2	13.4	1.5
17	Peterborough	9.4	12.5	1.3
18	Harrow (Windsor)	16.4	13.8	0.8
19	Dorset	8.8	9.1	1.0
20	Moosonee	2.6	2.7	1.0
21	Whiteface	8.6	12.1	1.4
22	Ithaca	13.3	9.7	0.7
23	Penn State	17.8	8.6	0.5
24	Virginia	11.9	5.6	0.5
25	Illinois	10.3	7.5	0.7
26	Brookhaven	12.8	8.5	0.7
27	Lewes	11.2	6.4	0.6
28	Oxford	12.7	7.0	0.6
29	Caribou	ME 3.9	5.8	1.5

TABLE 1 (Continued)

No.	Station Name		Predicted	Observed	OBS/PRED
30	Greenville	ME	5.1	5.9	1.2
31	Hubbard Brook	NH	7.8	6.8	0.9
32	Huntington Wildlife	NY	9.1	9.3	1.0
33	Aurora Research Farm	NY	12.6	13.3	1.0
34	Knobit	NY	12.3	10.5	0.8
35	Stillwell Lake-West Pt	NY	13.7	9.5	0.7
36	Leading Ridge	PA	17.8	9.4	0.5
37	Kane Exper. Forest	PA	16.8	11.9	0.7
38	Parsons	WV	18.4	14.4	0.8
39	Horton's Station	VA	12.2	9.5	0.8
40	Lewiston	NC	7.3	8.6	1.2
41	Research Triangle Park	NC	7.6	9.9	1.3
42	Finley (Raleigh)	NC	7.4	9.4	1.3
43	Clinton Crops Res. Sta.	NC	6.3	7.5	1.2
44	Piedmont Res. Station	NC	8.6	9.9	1.1
45	Coweeta	NC	8.6	8.5	1.0
46	Clemson	SC	7.7	7.8	1.0
47	Georgia Sta.	GA	7.1	8.1	1.1
48	Bradford Forest	FL	4.2	6.0	1.4
49	Austin-Cary Forest	FL	3.8	8.5	2.3
50	Walker Branch Watershed	TN	13.0	13.4	1.0
51	Caldwell	OH	19.9	16.1	0.8
52	Wooster	OH	16.5	12.3	0.7
53	Delaware	OH	12.1	13.3	1.1
54	Meridian	MS	5.6	6.3	1.2
55	SIU	IL	11.1	7.2	0.6
56	SALEM	IL	10.7	9.1	0.9
57	Bondville	IL	10.3	9.9	1.0
58	Argonne	IL	12.5	12.8	1.0
59	Kellogg Biological Sta.	MI	9.9	10.0	1.0
60	Wellston	MI	6.8	7.5	1.1
61	UMI Biological Sta.	MI	5.6	6.3	1.1
62	Trout Lake	WS	4.7	5.1	1.1

the model, the emissions were aggregated into 519 point sources. The emission strength of SO_4 was taken to be 2% of that for SO_2.

The wind speed u and f_θ correspond to a 600 m wind rose derived from rawinsonde observations made during the period 1972-1976 (Niemann, 1982). Observations from 67 stations were combined into 14 wind roses corresponding to different regions in the U.S. and Canada.

The average length of dry periods τ_d was chosen to be 100 hr on the basis of analysis performed by Henmi and Reiter (1978) and Niemann (1982). The dry removal rates λ_d and $\bar{\lambda}_d$ for SO_2 and SO_4 were based on a mixed layer height of 1000 m and a dry deposition velocity of 0.5 cms^{-1} and 0.05 cms^{-1} respectively. This translates to $\lambda_d^{-1} = 60$ hrs and $\bar{\lambda}_d^{-1} = 600$ hrs. The SO_2 to SO_4 conversion rate k_d was taken to be 1% hr^{-1}. Note that it is not possible to offer rigorous justification for the choice of these parameter values. However, these values are "consistent" with our knowledge of the processes related to these parameters.

Figure 5 shows a comparison between model predictions and observations. A "background" deposition of 2 kg/hec yr has been added to model estimates. This value has been used by Fisher (1978) in estimating sulfur deposition in Europe.

We see from the figure that the model performs well in explaining the observations. This comparison provides considerable support for the basic hypothesis that the removal of SO_2 (through in-cloud oxidation) in rain is rapid enough to allow us to neglect the details of the wet scavenging process. This simplification was first pointed out by Eliassen (1984). Because model estimates do not explicitly use rainfall amounts, the skill of the model does not depend upon the observed high correlation between rainfall amount and wet deposition.

As a further test of our SO_2 removal hypothesis, we compared observations with estimates of sulfur deposition based on the assumption that all the sulfur in rain corresponds to sulfate formed by gas phase oxidation of

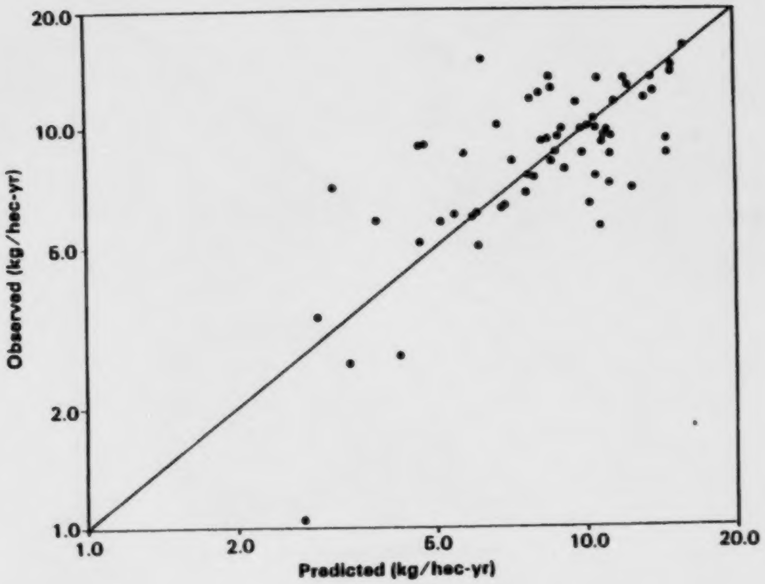

Figure 5. Comparison of model estimates with observations of annual wet sulfur deposition for 1980 at 62 stations listed in Table 1. Background of 2 kg/hec year has been added to model.

SO_2; SO_2 was not removed by rain. We see from Figure 6 that this assumption yields sulfur deposition estimates that are much smaller than the observations. This illustrates the role of our empirical model in suggesting that observations of wet deposition of sulfur point to the "efficient" removal of SO_2 by rain. Fisher and Clark (1983) reached the same conclusion by showing that estimates from a model similar to ours agreed best with observations when the removal rate of SO_2 was taken to be $\sim$ 40% hr^{-1}.

The second important hypothesis that forms the basis of our suggested model is that the wet deposition of sulfur is intimately related to the SO_2 emission distribution. In other words, we assume that emission distribution is a major contributor to the variance of the observed wet deposition pattern. To test this hypothesis we ran the model for two different emission distributions which were constructed as follows. North America was divided into two regions separated by the 95° meridian. The region that

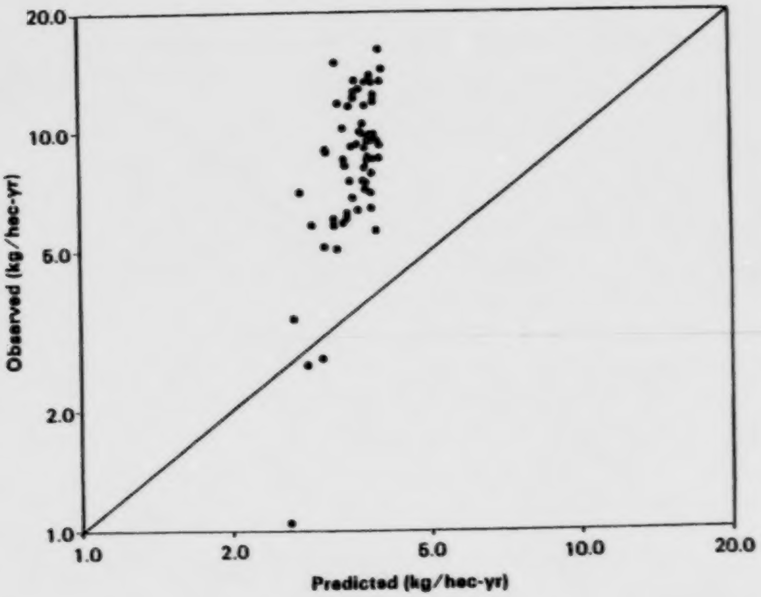

Figure 6. Same as Figure 2 except that only sulfate formed during dry periods contributes to sulfur in rain.

was east of this line was overlaid with a 1° x 1° grid. Point sources within each grid square were combined together and treated as a single point source located at the center of the square. A similar procedure was followed for the western part of the grid, except that the grid squares were chosen to be 2° x 2° to reflect the sparser emissions. The resulting emission distribution over North America was not very different from that corresponding to the base case consisting of 519 point sources. This is evident from the scatterplot of Figure 7 which differs little from that shown in Figure 5.

The second emission distribution was constructed by distributing the total SO_2 emissions uniformly over the grid system. The comparison between the resulting model estimates of wet deposition and observations is shown in Figure 8. It is clear that the pattern of observed sulfur deposition cannot be uncoupled with the emission distribution. This analysis illustrates the value of the model in interpreting observations.

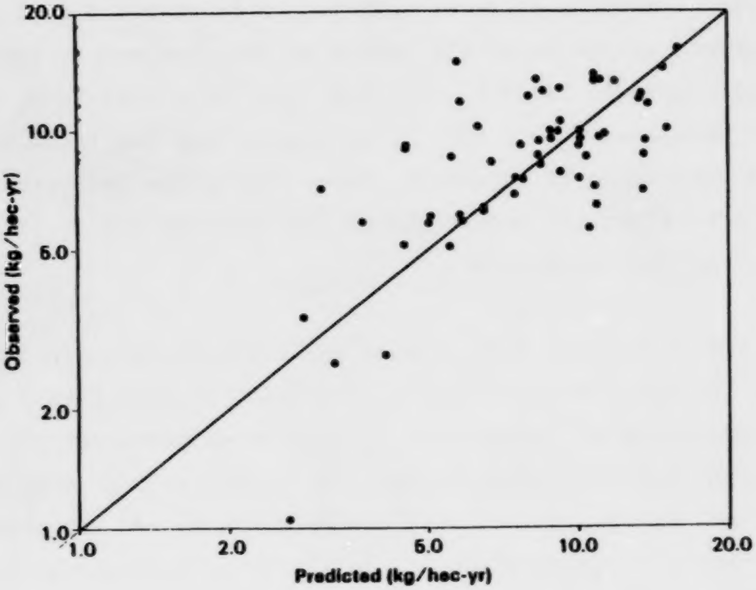

Figure 7. Comparison of model estimates with observations when emissions are gridded--see Text.

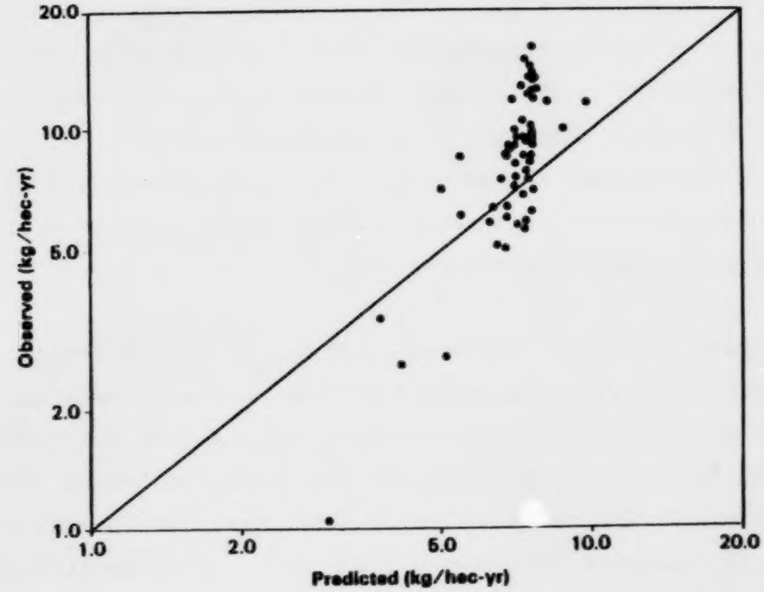

Figure 8. Same as Figure 4 except that emissions of sulfur are distributed evenly over the grid system.

A qualitative measure of model performance is provided by the geometric mean and standard deviation of the ratios of the observed to predicted deposition presented in Table 1. We find that the geometric $m_g = 1.13$ and the standard deviation $s_g = 1.65$. If we assume that the ratio of observed to predicted deposition is lognormal, these statistics indicate that for a given model prediction, we expect 95% of the observations to lie within a factor of 2.7 of this prediction.

Because the stochastic model relies so little on measured input, the variation of the observations about a prediction is most likely related to the unknown variation of the details of long range transport processes. We believe that the model provides an estimate of the average over an ensemble that is defined with respect to only the emission field. In other words, for a given emission distribution, s_g is likely to decrease as the averaging time increases. Because the details of meteorology cannot be predicted, the magnitude of s_g is not very relevant in using such a model to plan emission control strategy. Whether this type of model can be used for such an application is a question we will take up later.

A study by Fisher and Clark (1983) provides a detailed evaluation of the performance of the stochastic LRT model. A sensitivity analysis with the model showed that 1) the average rate of oxidation of SO_2 to sulfate cannot be much greater than 1% h^{-1}, or predicted ambient sulfate levels would be much higher than the corresponding observations, and 2) SO_2 removal in rain has to be efficient in the sense $\lambda_w \tau_w >> 1$ to explain the observed wet sulfur deposition pattern.

An important question considered by Fisher and Clark (1983) was that of linearity--are the model parameters functions of the concentration level? To answer this question they applied their LRT model to Europe and the ENA without changing the model parameters. The reasoning behind this exercise was the following. The ratio of the HC + NO_x emission to that of sulfur is much higher in Eastern North America than that over an equivalent area in Europe. This combined with the higher average solar intensity over ENA should translate into different levels of photochemistry over these two areas. Fisher and Clark (1983) asked the question: Do the model parameters have to vary to reflect the different chemistry in these two regions? The answer was a "no" as reflected in the results presented in Table 2.

The regression analysis was performed on the basis of the relationship,

$$\text{measured value} = a + b^{*}\ (\text{calculated value}) \qquad (23)$$

Model performance was more than satisfactory for all three sulfur components in both Europe and North America. Note that the model used the same parameters for both applications. It is interesting that the inferred background deposition (the intercept) has the same value of 0.3 $gSm^{-2}\ yr^{-1}$ in both areas. On the basis of results such as these, Fisher and Clark (1983) concluded that 1) the stochastic model provides a reasonable description of observed sulfur concentration and deposition patterns over both Europe and ENA, and 2) the sulfur system as a whole is not strongly non-linear. These conclusions are supported by Venkatram and Pleim (1984).

SUMMARY AND DISCUSSION

This paper reviews LRT models that are based on models for the probability of events associated with the long range transport and deposition of pollutants. There is sufficient evidence to indicate that stochastic LRT models are useful tools in the interpretation of observations of annually averaged concentrations and depositions of sulfur. There is reason to believe that nitrate patterns can also be examined with such models.

Can the stochastic LRT model be used to examine the effect of emission control strategy on sulfur deposition? To answer this question we notice that we can construct a "linear" model by assuming that $\lambda_w \tau_w >> 1$. This condition certainly holds for the present mix of pollutants found over ENA and Europe. A reduction in emission should be accompanied by an average increase in precipitation pH. Then it is reasonable to expect that this change will increase the efficiency of SO_2 wet removal, and the condition $_w\,{}_w >> 1$ would be strengthened. Perhaps, the stochastic LRT model can be used to examine the effect of reducing sulfur emission on wet sulfur deposition. It is important to note that these models have been successful

TABLE 2

COMPARISON OF CALCULATED AND MEASURED DATA
OBSERVATIONS SPAN THE PERIOD 1978-1980

(From Fisher and Clark, 1983)

Region	Europe	N. America
Airborne SO_2		
correlation coefficient	·84	·63
regression coefficients		
(a [μgm^{-3} SO_2], b)	(1.5, ·78)	(-4.6, 1.6)
Number of sampling sites	28	18
Airborne SO_4		
correlation coefficient	·69	·75
regression coefficients		
(a [μg m^{-3} SO_4], b)	29	18
Wet deposition (zero background)		
correlation coefficient	·61	·74
regression coefficients		
(a [g SO_4 m^{-2} $year^{-1}$|, b)	(1.4, 1.1)	(1.2, ·95)
Number of sampling sites	31	28
Wet deposition (background = 0.8 mg l^{-1} SO_4)		
correlation coefficient	·74	·72
regression coefficients		
(a, [g SO_4 m^{-2} $year^{-1}$], b)	(·17, 1.3)	(·64, ·89)
Number of sampling sites	31	28

only in explaining long-term sulfur deposition patterns. They have not yet been used to estimate the concentrations of other ions that contribute to rainfall acidity. It is possible that this admittedly empirical model is inherently incapable of describing acidity patterns.

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REFERENCES

Bolin, B. and C. Persson, 1975. Regional Dispersion and Deposition of Atmospheric Pollutants with Particular Application to Sulfur Pollution Over Western Europe. **Tellus**, **27**:281-310.

Fisher, B.E.A. and P.A. Clark, 1983. Testing a Statistical Long Range Transport Model on European and North American Observations. Paper presented at the 14th International Technical Meeting on Air Pollution Modeling and Its Application, Copenhagen.

Fisher, B.E.A., 1982. The Long Range Transport of Air Pollutants - Some Thoughts on the Present State of Modeling. Paper presented at the Joint Workshop on Ambient Air Pollution - Health Effects and Management, Schloss Laxenburg, Laxenburg, Austria, 27-30 July.

Fisher, B.E.A., 1978. The Calculation of Long-Term Sulfur Deposition in Europe. **Atmos. Environ.**, **12**:489-501.

Fisher, B.E.A., 1975. The Long Range Transport of Sulfur Dioxide. **Atmos. Environ.**, **9**:1063-1070.

Hamrud, M. and H. Rodhe, 1981. A Numerical Comparison Between Lagrangian and Eulerian Rainfall Statistics. **Tellus**, **33**:235-241.

Henmi, T. and E.R. Reiter, 1978. Regional Residence Time of Sulfur Dioxide Over the Eastern United States. **Atmos. Environ.**, **12**:1489-1496.

Lague, J.A., 1983. Acid Deposition Effects of Projected North American Emission Trends. ERT Report submitted to the Canadian Electrical Association, Montreal, Quebec, Contract No. 183 G271.

MOI, 1982. United States/Canada Memorandum of Intent, 1982. Emissions, Costs and Engineering Assessment - Final Report.

National Academy Press, 1983. Acid Deposition: Atmospheric Processes in Eastern North America. National Academy Press, 2101 Constitution Avenue, NW, Washington, DC 20418.

Niemann, B.L., 1982. The 1980 Data Set for Further Evaluation of Regional Air Quality/Acid Deposition Simulation Models. EPA Report, write to G. Foley, USEPA, ORD, Washington, DC 20460.

Patterson, D.E., R.B. Husar, W.E. Wilson and L.F. Smith, 1980. Monte Carlo Simulation of Daily Regional Sulfur Distribution: Comparison With SURE Sulfate Data and Visual Range Observations During August 1977. **J. Appl. Meteor.**, **20**:70-86.

Rodhe, H. and J. Grandell, 1972. On the Removal Time of Aerosol Particles from the Atmosphere by Precipitation Scavenging. **Tellus.**, **XXIV**:442-454.

Shannon, J.D., 1981. A Model of Regional Long-Term Average Sulfur Atmospheric Pollution, Surface Removal, and Net Horizontal Flux. **Atmos. Environ.**, **15**:689-701.

Slinn et al., 1979. Wet and Dry Deposition and Resuspension of AFCT/TFCT Fuel Processing Radionuclides. U.S. Department of Energy Final Report SR-0980-10, Air Resources Center, Oregon State University, Corvallis, Oregon.

Smith, F.B., 1981. Probability Prediction of the Wet Deposition of Airborne Pollution. **In**: Air Pollution Modeling and It's Application I, C. DeWispelaere (Ed.), Plenum Press, New York, 67-98.

Smith, F.B., 1981. The Significance of Wet and Dry Synoptic Regions on Long Range Transport of Pollution and Its Deposition. **Atmos. Environ.**, **15**: 863-873.

Stockwell, W.R. and J.G. Calvert, 1983. The Mechanism of the HO-SO_2 Reaction. **Atmos. Environ.**, **17**:2231-2237.

Tennekes, H., 1977. The General Circulation of Two-Dimensional Turbulent Flow on a Beta Plane. J. **Atmos. Sci.**, 34:702-712.

Venkatram, A. and J. Pleim, 1984. Analysis of Observations Relevant to Long Range Transport and Deposition of Pollutants. Submitted to **Atmos. Environ.**.

Venkatram, A. and J. Pleim, 1983. An examination of Linear Parameterizations in a Statistical Long Range Transport Model. Paper presented at the NATO/CMS 14th International Technical Meeting on Air Pollution Modeling and Its Application, Copenhagen.

Venkatram, A., B.E. Ley and S.Y. Wong, 1982. A Statistical Model to Estimate Long-Term Concentrations of Pollutants Associated with Long Range Transport. **Atmos. Environ.**, **16**, 249-257.

Wilson, W.E. and N.V. Gillani, 1979. Transformation During Transport: A State-of-the-Art Survey of the Conversion of SOă to Sulfate. Paper presented at the WMO Symposium on the Long Range Transport of Pollutants and Its Relation to General Circulation Including Stratospheric/ Tropospheric Exchange Processes, Sofia, Bulgaria, 1-5 October, 157-164.

CHAPTER V

METHODS FOR THE SENSITIVITY AND UNCERTAINTY ANALYSIS OF LONG RANGE TRANSPORT MODELS

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INTRODUCTION

In virtually all branches of science and engineering, mathematical models are used to describe the dynamics of complex systems. One direct consequence of using models is that some approximations are involved and these, in turn, lead to inevitable uncertainties in the predictions. Uncertainties can arise from several sources including the limited accuracy with which the underlying physical and chemical processes can be characterized and the inherent errors in measurements of the information needed by the model. Leaving aside, for the moment, the philosophical question of model validity the essential question in sensitivity analysis is to characterize the changes in system outputs that result from variations in either the input or structural parameters.

Conceptually the simplest approach to sensitivity analysis is to solve the system repeatedly while varying one parameter at a time and holding the others fixed. This type of approach, while easy to apply, soon becomes impractical as the complexity of the model and the number of parameters to be studied increases. In practice it is often critically important to identify those parameters that have the most impact on system performance. This need has lead to a considerable body of accumulated experience associated with the development and application of sensitivity analysis techniques to complex systems. For general background the reader is referred to the texts of Frank (1978), Tomovic (1963) and Tomovic and Vukobratovic (1972). More specialized literature reviews are available. Kramer et al. (1984), Rabitz et al. (1983) and Tilden et al. (1981) evaluated techniques suitable for use in chemical kinetics, Cacuci (1981ab), Cacuci et al. (1980, 1981) and Oblow (1971) describe procedures that have been applied to reactor safety problems. Methods for sensitivity analysis of electrical systems are presented in Parker (1971) and for control systems by Parker (1971). Gelinas and Vajk (1978) carried out a systematic study of methods suitable for use in air quality modeling.

A basic objective of this paper is to present a review and evaluation of those techniques that might be useful in a study of the effects of uncertainties in complex models of the form likely to be encountered in long range transport studies. Of particular interest are the models to be discussed at the workshop and those described in MOI (1982), NCAR (1983) and NRC (1983). Emphasis will be given to discussing both theoretical underpinnings of each technique as well as the practical implementation issues. In addition, a new method suitable for local sensitivity analysis of large systems of algebraic, differential and partial differential equations will be presented.

SENSITIVITY AND UNCERTAINTY ANALYSIS

Most of the models likely to be encountered in long range transport modeling can be represented in the compact form

$$\underline{N}[\underline{u}(\underline{x}),\underline{p}(\underline{x})] = \underline{F}[\underline{p}(\underline{x}),\underline{x}] \qquad (1)$$

where $\underline{x} = [x_1,\ldots,x_r]$ are the independent variables, $\underline{u}(\underline{x})$ is the n-dimensional state vector $= [u_1(\underline{x}),\ldots,u_n(\underline{x})]$, $\underline{p}(\underline{x})$ is a vector of the m system parameters $= [p_1(\underline{x}),\ldots,P_m(\underline{x})]$, $\underline{N}[\underline{u}(\underline{x}),\underline{p}(\underline{x})] = [N_1(\underline{u},\underline{p}),\ldots,N_n(\underline{u},\underline{p})]$ are nonlinear operators acting in general on the elements of the state vector and the components of the system parameters. For the purposes of the discussions to be presented below the elements of N can be considered to be difference, differential, algebraic or other types of operators. In (1) the term $\underline{F}[\underline{p}(\underline{x}),\underline{x}] = [F_1(\underline{p},\underline{x}),\ldots,F_n(\underline{p},\underline{x})]$ is a column vector whose elements represent the inhomogeneous source terms. As in the case of $\underline{N}[\underline{u}(\underline{x}),\underline{p}(\underline{x})]$ the elements of $\underline{F}$ may also be operators (rather than just functions) acting on the elements of $\underline{p}(\underline{x})$ and $\underline{x}$. If (1) is a differential operator there is also associated with the basic model a set of boundary and initial conditions of the form

$$\underline{B}[\underline{u}(\underline{x}),\underline{p}] = \underline{A}[\underline{x},\underline{p}] \quad \underline{x} \ \varepsilon \partial\Omega \qquad (2)$$

where $\partial\Omega$ is the boundary of the system.

The ultimate goal of any sensitivity analysis is to determine the form of the system output that results from the variations in the model input parameters. All feasible values of the parameter vector $\underline{p}(\underline{x})$ define the parameter space. Varying the parameters over their full domain, and solving the system (1), produces an n-dimensional response surface $\underline{u}(\underline{p},\underline{x})$. A typical example is shown in Figure 1 where the response of one state variable output $u_i(\underline{p},\underline{x})$ at $\underline{x} = (x_1,\ldots,x_r)$, to variations in the parameters $\underline{p} = (p_1,p_2)$ is shown. In this case the extent of the parameter domain is defined by the upper and lower limits for each of the variables p_1 and p_2. The point $u_i(\underline{p},\underline{x})$ represents the magnitude of $u_i(\underline{p},\underline{x})$ corresponding to the nominal parameter combination (p_1,p_2). In practice these nominal values typically represent best a priori estimates of the parameters.

So far in the discussion all the values of the parameters have been considered to be equally likely, however in most applications the parameters may have nonuniform probability distributions. While the response surface or sensitivity is independent of all assumptions about the likely parameter combinations, the expected or mean sensitivity depends on both the probability distribution for $\underline{p}$ and the response of the model. A sensitivity analysis then refers to the influence of parameter variations on the model predictions whereas a combined sensitivity/uncertainty analysis considers the additional factor of the parameter probability distributions.

An important assumption implicit in the above analyses is that both the surface $\underline{u}(\underline{p},\underline{x})$ and the response $\underline{R}[\underline{u},\underline{p}]$ were unique. One caution is clearly important. Establishment of the existence and uniqueness of solutions (and their derivatives) of complex nonlinear operators of the form (1) is a nontrivial exercise. For example, only limited results are available for the Navier Stokes equations which are perhaps the most commonly used mathematical descriptions of fluid flow. For the simple linear system $\{du/dt\}=[A]\{u\}$ it is possible to show that there are no parameter variations in the elements of $[A]$ that cause $\underline{u}(\underline{p},\underline{t})$ to have other than a unique solution (Crossley and Porter, 1979). On the other hand there are many equally simple systems that exhibit bifurcations as a result of their nonlinearity. For example, the system $\ddot{u}+1/2pe^{u}=0$, with $u(0)=u(1)=0$ has no smooth solution for $p>b$ where b is a positive constant, for $p=b$ there is exactly one solution and for $0<p<b$ there are two solutions. In the latter example the parameter value $p=b$ corresponds to a bifurcation point in the parameter space and at this point the character of the solution changes radically.

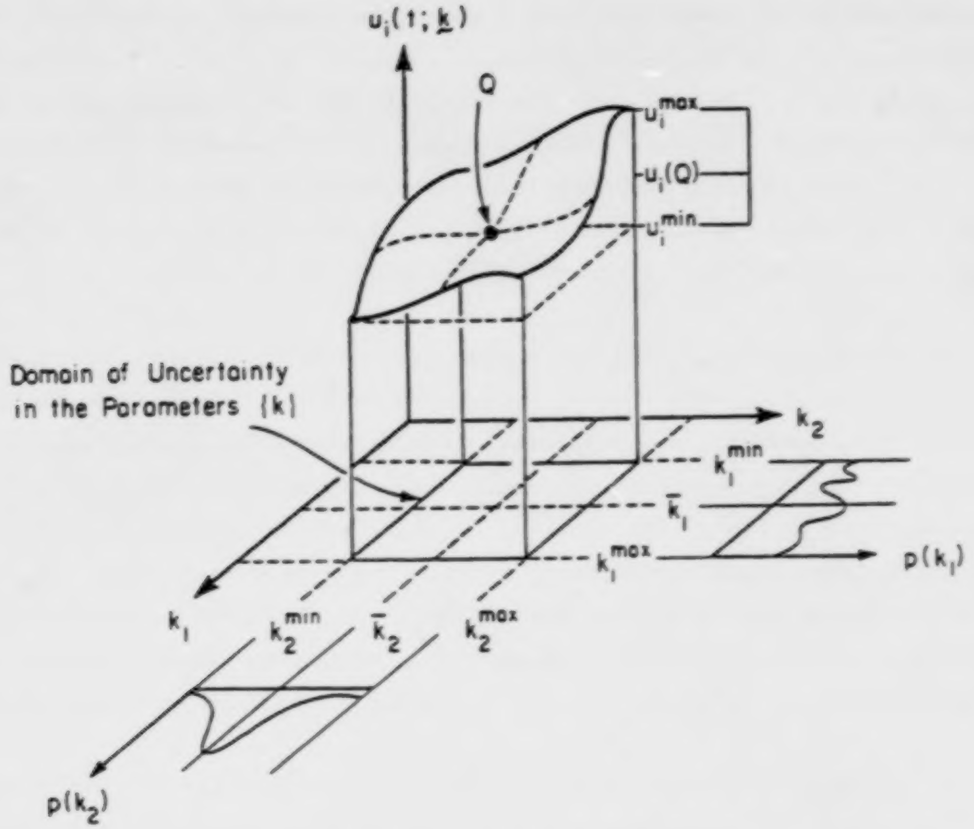
$u_i(t;\underline{k})$
Q
u_i^{max}
$u_i(Q)$
u_i^{min}
Domain of Uncertainty in the Parameters {k}
k_2
k_1^{min}
$\bar{k}_1$
k_1^{max}
$p(k_1)$
k_1
k_2^{min}
$\bar{k}_2$
k_2^{max}
$p(k_2)$

Figure 1. Schematic Representation of the Parameter Space k and the Response surface for state variable $u_i(t;k)$

Once the model has been established there are four basic elements that need to be considered when carrying out an analysis of the effects of changes in the parameters on the performance or predictions of the model. The key components are: the sensitivity measure or criterion, the extent of the parameter domain, the combined roles of sensitivity and uncertainty, selection of the appropriate technique and finally the computational cost. Subsequent sections of this paper are concerned with each of these issues.

SENSITIVITY ANALYSIS CRITERIA

There are, as might be imagined, many different measures of sensitivity. Perhaps the most elementary one is the change in system output $\delta\underline{u}$ that results from a parameter variation $\delta\underline{p}$ away from some nominal value p.

$$\underline{u} = \underline{u}(\underline{p}+ \underline{p}) - \underline{u}(\underline{p}) \tag{3}$$

In the form (3) the perturbation results in a point estimate of the sensitivity. If a sufficiently large number of parameter combinations are considered then it is possible to develop estimates of some important response statistics; the mean, variance and extrema of $\underline{u}(\underline{p})$. Similarly the information can also be used to develop a response surface approximation to $\underline{u}(\underline{p})$. The methodology implicit in (3) is often called scenario analysis and was used by Seigneur et al. (1981) to examine an airshed model. If the number of parameter perturbations and nominal values is small it is often possible to try all possible combinations. A moments reflection will indicate that the required number of model solutions grows very rapidly.

In practical applications it is useful to define a more general response measure that involves both the state variables as well as the parameters.

$$\underline{R}[\underline{u},\underline{p}] = \int_{\Omega} \underline{Q}[\underline{u}(\underline{x}),\underline{p},\underline{x}]\ \underline{dx} \tag{4}$$

where $\underline{Q}[\underline{u}(\underline{x}),\underline{p},\underline{x}]$ is a general function that may be defined as a distribution, differential operator or constant weight. For example, if the response is to be characterized in terms of the value of a particular state variable at the location $\underline{x}_o$ then (4) would be expressed in the form

$$\underline{R}[\underline{u},\underline{p}] = \int_{\Omega} \underline{u}(\underline{x})\delta(x-x)_o\ dx) \tag{5}$$

where $\delta(\underline{x}-\underline{x}_o)$ is the dirac delta. Similarly (4) can be used to define response variables that might represent fluxes through part or all of the system boundaries. Since most models will require numerical solution, the outputs needed to define the response surface will be only available for a finite set of parameter combinations. Given this situation the basic problem then becomes how to sample or characterize the response surface with sufficient regularity to adequately characterize $\underline{R}[\underline{u},\underline{p}]$. An analysis which accounts for the simultaneous variations in all the parameters over their full range of uncertainties is called a global method. Conversely, local analyses attempt to infer the shape or value of the response surface at a particular point. The limitations of local approaches are readily apparent, particularly if the model is highly nonlinear or the range of parameter variations is large.

A FUNCTIONAL ANALYSIS APPROACH TO SENSITIVITY ANALYSIS

In the interests of computational economy is often desirable to obtain as much information as possible from each model solution and parameter combination. One way to accomplish this objective is to use information about both the magnitude and shape of the response. While there are several different approaches to this task (perturbation theory, variational methods and differential techniques[1]) a common framework is provided through functional analysis. Most previous discussions of local sensitivity methods simply make use of the normal rules of differential calculus to derive the derivatives of the response with respect to the parameter values. For simple systems of algebraic or differential equations this approach is quite straightforward. When the underlying model is described by nonlinear operators the rules and approach to differentiation are no longer obvious. Fortunately there has been a great deal of theoretical activity directed at establishing the potential and limitations of local sensitivity analysis methods. For general background material on modern concepts in differentiation the reader is referred to Saaty (1981), Curtain and Pritchard (1977), Martin (1976) and Tapia (1971). The particular approach described below is based on the work of Cacuci (1981ab) and Cacuci et al. (1980, 1981).

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[1] In this paper the perturbation and variational approaches will not be considered. For further details about these techniques the reader is referred to Cacuci (1981ab), Koda et al. (1979a), Koda and Seinfeld (1982), Seigneur et al. (1982) and Tang and Pinder (1977, 1979). The variational approach, while theoretically appealing, is often extremely cumbersome to implement and as a result it is usually not a viable method for complex multi-dimensional problems.

Given the system response $\underline{R}(\underline{u},\underline{p})$ and the model of the physical system $\underline{N}[\underline{u}(\underline{x}),\underline{p}(\underline{x})]=\underline{F}[\underline{p}(\underline{x}),\underline{x}]$ the variation or change in $\underline{R}$, $\delta\underline{R}$ due to a parameter change $\delta\underline{p}$ is given by

$$\delta\underline{R} = \int_{\Omega} \underline{Q}'_{\underline{u}}\, \delta\underline{u}(\underline{x})\, \underline{dx} + \int_{\Omega} \underline{Q}'_{\underline{p}}\, \delta\underline{p}(\underline{x})\, \underline{dx} \qquad (6)$$

where $\underline{Q}'_{\underline{u}}$ and $\underline{Q}'_{\underline{p}}$ are vectors whose components represent Frechet derivatives of $\underline{Q}$ with respect to the state variables $\underline{u}$ and the parameter values $\underline{p}$. The first term in (6) accounts for the variation in $\delta\underline{R}$ that results from changes in the state variables and since $\underline{u}=\underline{u}[\underline{p}(\underline{x}),\underline{x}]$ the first term also implicitly depends on the parameter variations. The second term in (6) accounts for the direct changes in $\underline{R}$ that result from parameter changes.

There are several ways to define a Frechet derivative, the form adopted below is due to Tapia (1971) and Cacuci et al. (1980). Let X and Y be two real Banach spaces, and T be a general operator T:X->Y. If is a real number, and x S then if

$$\lim_{\varepsilon\to 0} \left\| \frac{T(x+h) - T(x)}{\varepsilon}\, T(\underline{x},h) \right\| = 0 \qquad (7)$$

holds for all vectors $\underline{h}\in X$, $\underline{T}(\underline{x},\underline{h})$ is called the Gateaux variation of T at $\underline{x}$ with increment $\underline{h}$. The value T is linear and bounded in $\underline{h}$ if and only if T satisfies a weak Lipschitz condition at $\underline{x}$, and $T(\underline{x}+\varepsilon\underline{h}_1+\varepsilon\underline{h}_2)-T(\underline{x}+\varepsilon\underline{h}_2)+T(\underline{x}) = \theta(\varepsilon)$, where $\theta(\varepsilon)\to 0$ as $\varepsilon\to 0$. In this case, $T(\underline{x},\underline{h})=DT(\underline{x},\underline{h})$, where $DT(\underline{x},\underline{h})$ is called the Gateaux differential of T at $\underline{x}$. The value $DT(\underline{x},\underline{h})$ also defines an operator T'_x (acting on $\underline{h}$) of the space of bounded linear operators from X to Y and this operator is called the Gateaux derivative of T at $\underline{x}$. If at the point $\underline{x}X$,

$$T(\underline{x}+\underline{h}) - T(\underline{x}) = dT(\underline{x},\underline{h}) + w(\underline{x},\underline{h}) \tag{8}$$

where

$$\lim_{\|\underline{h}\| \to 0} \frac{\|\underline{w}(\underline{x},\underline{h})\|}{\|\underline{h}\|} = 0 \tag{9}$$

then $dT(\underline{x},\underline{h})$ is called the Frechet differential of T at $\underline{x}$. If dT exists, it corresponds to a bounded linear operator on $\underline{h}$ called the Frechet derivative T'_x, and $dT(\underline{x},\underline{h})=T'_x\underline{h}$. The Frechet differential has the usual properties of the classical differential of a function of one or several variables, in particular the chain rule applies. Further, the definition (9) also forces an explicit recognition that the results depend on the norms adopted for X and Y. If the Gateaux differential $DT(\underline{x},\underline{h})$ exist for all $\underline{x}$ in a neighborhood of $\underline{x}_o$ and is continuous at $\underline{x}_o$, then $dT(\underline{x}_o,\underline{h})$ exists and is equal to $DT(\underline{x}_o,\underline{h})$. In subsequent sections of this paper it will be assumed that the Frechet derivative exists. In practice, the stronger conditions implied by the existence of the Frechet derivative are also needed to ensure convergence of the numerical solution procedures used to solve the governing model.

Returning now to (6) it can be seen that in order to evaluate the sensitivity, the vector $\delta\underline{u}$ is required. Using the notions introduced above, $\delta\underline{u}$ can be found by taking the Frechet differentials of the basic system model (1) to give

$$\underline{Q}'_u \; \underline{u} = [\underline{F}'_p - \underline{N}'_p] \; \underline{p} \tag{10}$$

One important point to note is that the operator $\underline{Q}'_u$ is linear even if the underlying model itself is nonlinear. Simply stated the Frechet derivative produces the best linear approximation to the response surface at the point corresponding to the nominal parameter combination. Unfortunately if the number of parameters to be considered is large relative to the number of state variables then solving (10) to obtain the desired sensitivity information may consume an excessive amount of computational resources. An alternative approach is based on the recognition that the sensitivity equation (10) is linear and so an adjoint formulation of the problem is possible.

For a general operator $\underline{L}$ its adjoint $\underline{L}^*$ is defined by

$$\langle \underline{L}^*\underline{v}, \underline{u} \rangle = \langle \underline{v}, \underline{L}\,\underline{u} \rangle + \underline{P}[\underline{v}, \underline{u}] \tag{11}$$

where the vector $\underline{v} = [v_1, \ldots]$ belongs to the domain of $\underline{L}^*$, and $\underline{P}$ is a term that arises because of the boundary conditions. The inner products <,> in (11) are given by

$$\langle \underline{v}, \underline{u} \rangle = \int_{\Omega} \underline{u} \cdot \underline{v} \; d\underline{x} \tag{12}$$

As noted by Cacuci et al. (1980) the existence and introduction of the adjoint operator $\underline{L}^*$ makes it possible to recast the expression for $\underline{R}$ in terms of the solution $\underline{v}$ of an adjoint system that is independent of $\delta\underline{u}$, $\delta\underline{p}$, and the Frechet derivatives with respect to $\underline{p}$. The steps in the process are as follows. First, the adjoint system is formally written as

$$\underline{L}^*\underline{v} = \underline{S}^* \tag{13}$$

where the terms in $\underline{L}^*$ are derived from (11) using the inner product definition (12), and $\underline{S}^*$ is the adjoint associated with $\underline{S}=\underline{F}'_p-\underline{N}'_p$. Under the proper conditions the adjoint boundary conditions can be formed if they are independent of $\delta\underline{x}$, $\delta\underline{u}$ and the Frechet derivatives with respect to $\underline{p}$ and finally all terms in $\underline{P}[\underline{v},\delta\underline{u}]$ that contain the unknown value of $\underline{u}$ vanish on the boundary. Under these conditions then it can be shown that the variation in $\underline{R}$ is given by

$$\delta\underline{R} = \int_{\Omega} \{\underline{Q}'_p + \underline{v}[\underline{F}'_p - \underline{N}'_p]\} \; \delta\underline{p}(\underline{x}) \; d\underline{x} + \hat{\underline{P}}[\underline{v},\delta\underline{u}] \tag{14}$$

The final result, is independent of $\delta\underline{u}$ and since (13) does not depend on $\delta\underline{p}$, one adjoint calculation provides all the necessary information for all the parameters. So by solving the basic model (1) in conjunction with its adjoint, the response variation can be determined for any parameter change $\delta\underline{p}$. In passing it is important to point out that $\underline{v}$ is adjoint to $\delta\underline{u}$ and not to the state function $\underline{u}$. For many practical problems $\delta\underline{p}$ is a constant, and the contribution from the boundary terms can be ignored. As a result (14) can be written in the simpler form

$$\delta\underline{R} = {}_{\Omega}\!\int \{\underline{Q}'_p + \underline{v}[\underline{F}'_p - \underline{N}'_p]\}\, d\underline{x}\,\delta\underline{p}(\underline{x}) \tag{15}$$

The integral in (15) is frequently referred to as the sensitivity derivative dR/dp. Because of the wide dynamic range that may be encountered it is often useful to normalize the derivative to the form (p/R)dR/dp.

Two basic approaches to differential sensitivity have been defined in this section for general systems of nonlinear operator equations. If the number of parameters is small then the direct solution of (1) and (10) can be used to obtain the desired sensitivity information. When there are a large number of parameters then the adjoint formulation provides a more economical approach by solving (1) and its adjoint (13), and then, applying the results in (14) to evaluate the influence of parameter variations. While the adjoint formulation has the desirable feature that the computational cost may be reduced it is important to point out that considerable effort may be required to develop the numerical solution procedures compatible with (13, 14).

DIRECT AND ADJOINT METHODS FOR LOCAL SENSITIVITY ANALYSIS

In the previous section a general framework was introduced for determining the response sensitivity of a wide class of nonlinear operators. The type of models likely to be encountered in long range transport are usually of three basic forms

$$\text{Algebraic} \qquad \underline{N}(\underline{u},\underline{p}) = \underline{0} \tag{16}$$

$$\text{Differential} \qquad \underline{N}(\underline{u},\underline{p}) = \frac{d\underline{u}}{dt} - \underline{f}(\underline{u},\underline{p},\underline{t}) = \underline{0} \tag{17}$$

Distributed $$\underline{N}(\underline{u},\underline{p}) = \frac{\partial \underline{u}}{\partial t} - \nabla\cdot(\underline{vu}) - \ldots - \underline{F}[\underline{u},\underline{p},\underline{t}] = \underline{0} \qquad (18)$$

From the point of view of actually carrying out a sensitivity analysis it is usually only necessary to consider models of the form (17). The reason for this is that (16) is a special case of (17) and the distributed parameter models usually can be replaced by a semi-discrete approximation at a finite number of spatial locations. Most finite difference, finite element or collocation methods, when applied to (18), result in systems of ordinary differential equations of the form

$$[\underline{R}(\underline{p})]\ \{\frac{d\underline{u}}{dt}\} + [\underline{S}(\underline{p})]\{\underline{u}\} - \underline{F}[\underline{u},\underline{p},t] = \underline{0} \qquad (19)$$

where the elements of the matrices $[\underline{R}(\underline{p})]$ and $[\underline{S}(\underline{p})]$ depend on the particular numerical solution technique. For example, if simple finite difference methods are used $[\underline{R}(\underline{p})]$ will be a diagonal matrix, if higher order finite element basis functions are employed to approximate $\underline{u}$ then $[\underline{R}(\underline{p})]$ will have sparsely distributed elements.

Give the basic model (17) the operator can be differentiated, using the Frechet derivatives introduced in the previous section, to give the sensitivity equation

$$\underline{N}'_u\ \{\frac{\delta \underline{u}}{\delta \underline{p}}\} + \underline{N}'_p = 0 \qquad (20)$$

where

$$\underline{N}'_u\,\cdot = \frac{d}{dt}(\cdot) - (\frac{\delta \underline{f}}{\delta \underline{u}}) \qquad (21)$$

and

$$\underline{N}'_p = -(\frac{\delta \underline{f}}{\delta \underline{p}}) \qquad (22)$$

For the case of constant parameters and continuous derivatives the sensitivity equation (20) is given by the nxm matrix differential equation

$$\frac{d}{dt}[S] - [J][S] - \frac{\delta \underline{f}}{\delta \underline{p}} = 0 \qquad (23)$$

where [S] is the nxm matrix of linear sensitivity coefficients

$$S_{ij}(t) = \frac{\delta u_i}{\delta p_j} \tag{24}$$

and [J] is the nxn Jacobian matrix

$$J_{ij}(t) = \frac{\delta \underline{f}_i}{\delta \underline{p}_i} \tag{25}$$

A typical column of [S] denotes the sensitivity of $\underline{u}$ with respect to the j-th parameter p_j. The initial conditions for the system (23) are given by [S(0)]=[0] unless any $u_i(0)$ are included in the parameter vector in which case the appropriate terms in [S(0)] are set to unity. As noted in the previous section (23) is linear and, since there is no direct coupling between each of the m vector differential equations, each column can be solved independently. Edeleson et al. (1981) utilized the latter observation to implement a high speed solution on a vector processing computer system.

A. Coupled Solution of System and Sensitivity Equations

Given the model equations (17) and the associated sensitivity equations (23) there are a variety of ways to obtain the desired sensitivity information. The simplest involves a direct solution of the coupled system of n(m+1) ordinary differential equations defined by (17) and (23). This method was used by Dickinson and Gelinas (1976) and Atherton et al. (1975). In general, solving the complete system is usually plagued with numerical difficulties even though there are efficient procedure for calculating higher order derivatives if they are needed (Barhen and Cacuci, 1980).

Operationally it is somewhat more convenient to consider the parameters one at a time; if this approach is adopted the number of required solutions increases to 2nm. This number can be reduced if the intermediate results from the solution of (17) are saved and used to help solve (23). While the three approaches produce similar results they can involve considerably different computational costs: $O[n^3(m+1)^3]$ for the coupled system, $O[m(2n)^3]$ for the one parameter at a time case and $O[(m+1)n\ ]$ for the interpolated solution. Since the equations of interest are usually stiff, and m(>n) is in general quite large, the above procedures can be quite expensive.

B. Adjoint Methods for Solving the Sensitivity Equations

Quite clearly if the number of parameters is large the computational cost of repeatedly solving the system model can be prohibitive. An economical alternative is possible. As noted in section 2 if the Frechet derivatives of the basic model exist and certain conditions are satisfied on the system boundaries then it is feasible to construct an adjoint formulation of the sensitivity analysis problem. Once the model and the adjoint equation has been solved then it is a simple task to derive any number of parameter sensitivities.

Since the system (23) is a linear inhomogeneous equation with time varying coefficients, it can be solved by first calculating the solution of the homogeneous part and then determining the particular solutions corresponding to each parameter. This method has been extensively developed by Hwang et al. (1978), Dougherty et al. (1979), Hwang (1982) and Dermilap and Rabitz (1981ab), the discussion below is based on Rabitz et al. (1983).

The homogeneous problem can be written

$$\frac{d}{dt}\underline{K}(t,t') = \underline{J}(t)\,\underline{K}(t,t') \qquad (26)$$

where $\underline{K}(t',t')=I$ and $t>t'$. The nxn Green's Function matrix $\underline{K}$ contains the n-linearly independent solutions admitted by (26). Once $\underline{K}$ has been established then the full solution of the sensitivity equation (23) is given by

$$[S(t)] = [K(t,0)][S(0)] + \int_0^t [K(t,t')]\,[B]\,dt' \qquad (27)$$

where the matrix [B] contains the inhomogeneous term on the left hand side of (23). Note that in the integral the first argument of $\underline{K}$ is fixed while the second is varying. An efficient method for solving the system (27) is to use the adjoint Green's function defined by

$$\frac{d}{dt}\underline{K}^* (t,t') = -\underline{K}^*(t,t')\underline{J}(t') \qquad (28)$$

where $\underline{K}^*(t,t)=I$ and $t'<t$. The adjoint is solved backward in time and then the property $\underline{K}^*(t',t)=\underline{K}(t,t')$ is applied in (27) by making use of the group property $\underline{K}(t_3,t_1)=\underline{K}(t_3,t_2)\underline{K}(t_2,t_1)$. The major advantage of the adjoint formulation is that the sensitivity integrals (27) can be more easily evaluated row by row as function of t' at a fixed time t. The calculations needed to evaluate the Green's functions are independent of the number of parameters.

Recently Kramer and Calo (1981) improved the basic Green's Function method in several important ways. They made use of the piecewise Magnus method (Magnus, 1954) to solve for the Green's function, an analytic approximation to solve the sensitivity integrals and, most significantly, made the resulting computer programs publicly available (Kramer et al., 1982). To date the algorithm of Kramer et al. has been primarily used for sensitivity analysis of kinetic mechanisms. Other applications of the adjoint function approach include: a study of alkane pyrolysis by Edelson and Allara (1980), hydrogen-oxygen combustion by Dougherty and Rabitz (1980), the movement of maximum responses by Maudlin et al. (1981), a study of reactor safety codes by Parks and Mudlin (1981). In summary the adjoint formulation offers the potential for large savings in computational costs over direct methods when the number of parameters is large.

THE DIRECT DECOUPLED APPROACH TO SENSITIVITY ANALYSIS

While the direct sensitivity method has the advantage of simplicity and the adjoint procedure is efficient when there are a large number of parameters neither are particularly satisfactory for complex systems. The direct method suffers because of its high computational cost. While the adjoint formulation is cheaper the solution of the Green's function and the associated sensitivity integrals can involve a considerable amount of additional computer programming beyond that needed to solve the basic model. Recently a new approach called the direct decoupled method has emerged. The technique is based on the recognition that much of the numerical effort required to solve the basic model can be used in the sensitivity analysis.

Consider, for example, the nonlinear algebraic model (16). If the parameters are constants then the sensitivity equation (20) can be solved to give

$$[J][S] = -[B] \tag{29}$$

where as before [S] is the matrix of parameter sensitivities, [J] is the Jacobian matrix, and [B] is formed from $\partial \underline{N}/\partial \underline{p}$. Now in practical problems the model (16) will require numerical solution, and the most common procedure is Newton's method.

$$[J]\{\underline{u}_{m+1} - \underline{u}_m\} - \{\underline{N}(\underline{u}_m,\underline{p})\} \tag{30}$$

where the subscript m denotes the iteration number. Most of the work in using Newton's method involves the LU decomposition of [J] that is needed to solve (30) for the increment $\{\underline{u}_{m+1} - \underline{u}_m)\}$. Quite clearly, once the system (30) has converged to the solution, the sensitivity coefficients can be obtained by one additional matrix multiplication. An alternative way to view this example is that the sensitivity information can be obtained by differentiating the numerical approximation to the solution of the basic model. This idea has been suggested by a number of previous investigators including: Kelley and Denham (1969), Dunker (1980, 1984) and Leis and Kramer (1984).

Consider a general system of the form

$$\underline{N}(\underline{u},\underline{u},\underline{p},\underline{t}) = 0 \tag{31}$$

This set of equations, like the simpler algebraic form, is also normally solved using Newton's method.

$$[J]\{\underline{u}_{m+1} - \underline{u}_m\} = -\{\underline{N}[\underline{u}_m\underline{u}_m,\underline{p})\} \tag{32}$$

the only difference being the presence of the temporal derivative in the right hand side term. There are several ways to develop a numerical approximation for the derivatives du/dt, the particular method adopted here, for illustrative purposes, is to use the classic Gear backward difference formulae. In general there are a wide range of applicable formulae (see, for example, Kelley and Denham, 1969 and McRae, 1984). The temporal derivative in (32) can be replaced by

$$\dot{u}(t_n) = \frac{1}{hb_o} [u_n - \sum_{j=1}^{k_1} a_j u(t_{n-j}) - h \sum_{j=1}^{k_2} b_j \dot{u}(t_{n-j})] \qquad (33)$$

where the constants k_1, K_2, a_j and b_j are characteristic of the particular method and h is the time step. Note that the underbars indicating vectors have been dropped for notational convenience. The expression (33) can be differentiated with respect to the parameters p to produce a replacement for the temporal derivatives that appear in (23). This latter step is important because the sensitivity equations now become explicit algebraic expressions, in other words the coupled system of differential equations (17) and (23) no longer has to be solved.

The method of solution is quite straightforward and easy to implement. First, the solution of the model (17) is advanced a time step from t to t+h by solving the system of nonlinear equations associated with the Gear algorithm. For example, if backward difference formulae are used, the Newton iteration takes the form

$$[I-hb_oJ]\{u_{n(M+1)} - u_{n(m)}\} = - \{u_n - hb_o \underline{f}(\underline{u}_n, \underline{p}, t_n) - \sum_{j=1}^{q} a_j u(t_{n-j})\} \qquad (34)$$

At the end of a successful step the LU decomposition of [I-hboJ] is saved and used to solve for the parameter sensitivities that are given by the explicit expressions

$$[I-hb_oJ][S] = hb_o \frac{\delta \underline{f}}{\delta \underline{p}} + \sum_{j=1}^{q} a_j \, [S(t_{n-j})] \qquad (35)$$

Once the parameter sensitivities have been determined then the next step is to solve the model equations forward in time for another time step. The method is direct in the sense that both the model and sensitivity equations are solved in the forward direction but decoupled because the sensitivities are calculated at the end of each successful time step.

The computational experience of Dunker (1984) and McRae (1984) indicate that the direct decoupled approach offers a very viable tool for sensitivity analysis. The method is extremely easy to implement since it only requires relatively minor modifications to the computer code used to solve the basic model. This is in sharp contrast with the effort required to use either adjoint or variationally based approaches. An additional factor is that the direct decoupled method is much faster and more stable than the Green's function technique on problems of comparable complexity.

GLOBAL METHODS FOR SENSITIVITY AND UNCERTAINTY ANALYSIS

In the previous sections the basic objective was to characterize the output response of the model in the vicinity of the nominal parameter values. Often the parameter uncertainties are such that it is desirable to characterize the response surface over wider ranges of $\underline{p}$. In carrying out such analyses, the basic consideration to keep in mind is to minimize the number of model solutions. As in the discussion of the simple sensitivity measure (3) simply varying the parameters one at a time in not particularly useful especially if m is large. For example, consider a model with m parameters each with r different discrete values. The systematic evaluation would require $O(m^r)$ solutions of the basic model and even relatively small values of m can render the approach infeasible. The key to a successful global method is to devise an economical means for sampling the parameter space.

A. Monte Carlo Methods

Perhaps the most well known sampling procedure is the Monte-Carlo method. In this procedure the parameter combinations are selected at random from the $\underline{p}$ space. One major advantage of the Monte Carlo method is that it can be readily adapted to situations in which one or more of the parameters have known distributions. Stolarski et al. (1978) used Monte Carlo procedures to study the effects of propagation of uncertainties in reaction rate constants on the predictions of a stratospheric ozone model. The uncertain rate constants were assumed to be lognormally distributed about the mean of measured values. The computational procedure adopted in their work was to continue to sample from the parameter space until the statistics of the sensitivity measures stabilized.

B. Stratified and Pattern Search Methods

What is often not realized is that the value of Monte Carlo methods is not the randomness of the sampling but the resulting equidistribution properties of the sets of points in the parameter space. Once it is recognized that the primary objective of a Monte Carlo procedure is to produce a uniform distribution of points in the parameter space, then pattern search methods become a viable global sensitivity analysis method. The brute force method for distributing points is far from optimal. Consider the two dimensional cases shown in Figure 2. While the two distributions employ the same number of points the degree to which the parameter space is filled is radically different. Techniques of the type described in Aird and Rice (1977) and Mackay et al. (1979) can be used to lower the number of sample points beyond that need in a Monte Carlo search. One of the more widely known techniques is Latin hypercube sampling. In this approach the parameter space sampling tends to be more uniform and the outputs, while random, are not completely independent samples.

C. Fourier Amplitude Sensitivity Test

An alternative global sensitivity analysis method is the Fourier Amplitude Sensitivity Test (FAST) introduced by Cukier et al. (1973, 1975 and 1978), and Schaibly and Shuler (1973). The essence of this technique is to assign periodic functions of a new variable, s, to each of the parameters.

$$P_j = P_j + v_j \sin(w_j s), \; j=1,\ldots,n \tag{36}$$

where $o<s<2\pi$ and the p_j are the nominal parameter values, v_j is a positive constant chosen such that the parameter values are between assigned upper and lower limits. Under certain conditions each new value of s defines a

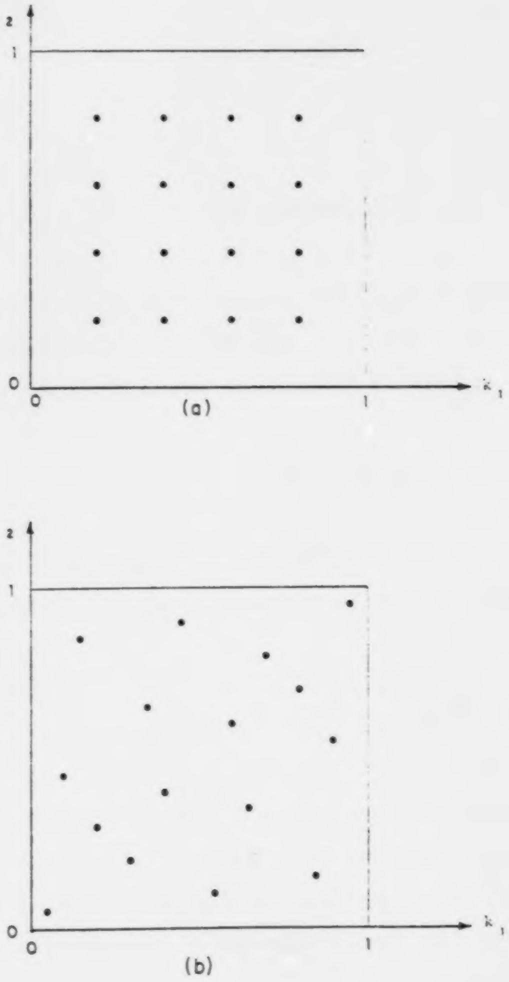

Figure 2. Systematic search patterns of parameter space.

unique parameter combination along a search curve that can be made to pass arbitrarily close to any point in the parameter space. The set of integer frequencies $\{w_j\}$, are chosen to closely approximate an incommensurate distribution in which there are no interferences. Using the parameter distribution (36) the model is solved at uniformly spaced values of s to give a set of outputs $\underline{u}(s)$ which in turn can be subjected to a Fourier analysis. By sampling u(s) along the search curve and performing a discrete Fourier analysis it is possible to determine the contribution of individual parameters to the global sensitivity. The Fourier components are defined as

$$A_k^{(i)} = \frac{1}{\pi} \int_o^{2\pi} u_i\ (s)\ \sin(ps)\ ds \qquad (37)$$

and

$$B_k^{(i)} = \frac{1}{\pi} \int_o^{2\pi} u_i\ (s)\ \cos(ps)\ ds \qquad (38)$$

where the subscript k is a particular frequency associated with parameter uk. Using Parseval's theorem, the total variance of the model output arising from all the different parameter combinations is given by

$$\delta^2 = \frac{1}{2} \sum_{k=1}^{\infty} (A_k^{\ 2} + B_k^{\ 2}) \qquad (39)$$

If the Fourier coefficients (37) and (38) are evaluated at the fundamental frequencies of each of the parameters then the variance

$$\delta^2_{wk} = \frac{1}{2} \sum_{p=1}^{\infty} (A_{pw_k}^{\ \ 2} + B_{pw_k}^{\ \ 2}) \qquad (40)$$

is that part of the total variance δ^2 in the output that corresponds to uncertainty arising from the k-th parameter. The ratio of (40) and (39) is a normalized sensitivity measure called the partial variance that allows relative ranking of the importance of each parameter.

The method has been primarily used in chemical kinetics and some typical applications are described in: Boni and Penner (1976), Falls et al. (1979) and Koda et al. (1979b). Recently the technique has been extended to variables that have only one of two states (Pierce and Cukier, 1981).

D. Stochastic Sensitivity Analysis

One additional technique for global sensitivity analysis is to consider that the variation in parameter values about their "true" values can be represented by means of a probability distribution. The most general statement of the sensitivity/uncertainty problem then becomes how to determine the probability distribution of the model outputs given the input distribution. Some initial steps towards a solution have been made by Costanza and Seinfeld (1981) and Tilden et al. (1981) by studying the Liouville-like equations that arise for systems of ordinary differential equations. If $\underline{P}(\underline{u},t)$ is the probability distribution for the model output then it is possible to show that for systems of the form (17) that $\underline{P}(\underline{u},t)$ is described by

$$\frac{\delta}{\delta t}\underline{P}(\underline{u},t) = \nabla_y \cdot \{[f(u,t)]P(u,t)\} \tag{41}$$

While at this time only limited results are available for very simple kinetic systems the method offers considerable potential.

BOUNDING ANALYSIS

Frequently the objective of a combined sensitivity/uncertainty analysis is to establish the likely limits of model output values. One technique that is often ignored is the use of linear programming. For example consider the linear system

$$[A]\{u\} = \{b\} \tag{42}$$

where the elements of both $[A]$ and $\{b\}$ are uncertain. The key question is what are the upper and lower limits of $\{u\}$ given the uncertainties in the model parameters. If the perturbations to $[A]$ and $\{b\}$ are expressed in the form

$$[A] - [A(p)] \leqslant [A] \leqslant [A] + [A(p)] \tag{43}$$

and

$$\{b\} - \{b(p)\} \leqslant \{b\} \leqslant \{b\} + \{b(p)\} \tag{44}$$

where $[A(p)]$ and $\{b(p)\}$ are the perturbations then it is a relatively straightforward task to set the bounds on $\underline{u}$. If the signs of $\underline{u}$ are known it is feasible to set the upper and lower limits by solving the linear programs

$$\begin{array}{ll} \max & c_j . q \text{ (upper bound)} \quad -c_j . q \text{ (lower bound)} \\ \text{s.t.} & \{[A][S] - [A(p)]\}\{q\} \leq \{b\} + \{b(p)\} \\ & \{-[A][S] - [A(p)]\}\{q\} \leq -\{b\} + \{b(p)\} \\ & \{q\} \geq 0 \end{array} \qquad (45)$$

where

$$\{q\} = [|u_1|, \ldots, |u_n|]$$

and

$$c_j = [0, \ldots, 0, \mathrm{sgn}(u_j), 0, \ldots 0]$$

The elements of the diagonal matrix [S] are given by $\mathrm{sgn}(u_i)$, $i=1,\ldots,n$. Further details of the algorithm are contained in Cope and Rust (1979), Kato (1966), Kilkas and Hutchison (1980) and in Milford and McRae (1984). In the latter work, the formulation has been used to set bounds on emission controls given uncertainties in air quality measurements and the elements of the source receptor model resulting from meteorological variability. The basic ideas embodied in this bounding analysis can also be extended to non-linear systems. Cacuci et al. (1980) have used bounding analyses in nuclear reactor problems and Kilkas and Hutchinson (1980) for chemical process design.

COMPUTATIONAL CONSIDERATIONS

From a practical point of view a dominant consideration in selecting an appropriate analysis method is the computational cost. When comparing the techniques presented above, and summarized in Figures 3 and 4.

It is important to keep in mind two basic considerations: one is simply the number of times the model must be solved to obtain the desired sensitivity information. The second factor, which is often overlooked in practice, is the additional resources that may be required to implement the particular technique. For example, some techniques do not require extensive programming beyond that needed to solve the basic model while others can require considerable additional effort. While the cost of each model solution can be expressed in terms of the required number of solutions the final choice of analysis method will often be dictated by the complexity of

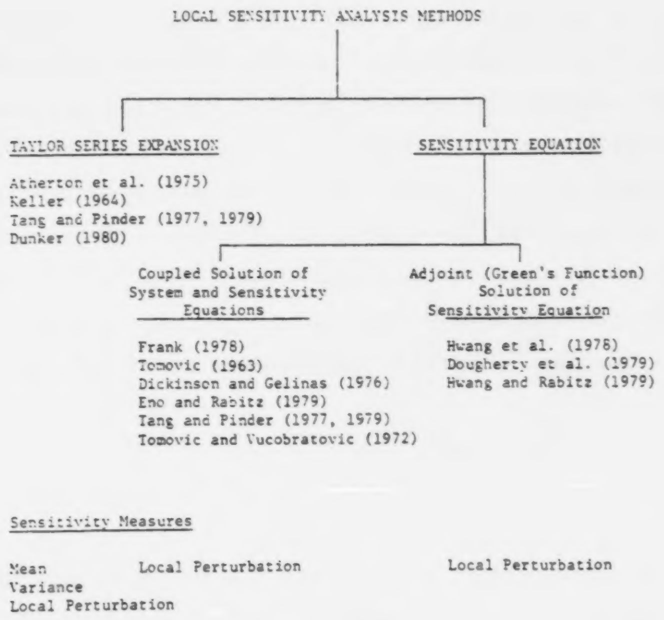
LOCAL SENSITIVITY ANALYSIS METHODS
TAYLOR SERIES EXPANSION
Atherton et al. (1975)
Keller (1964)
Tang and Pinder (1977, 1979)
Dunker (1980)
SENSITIVITY EQUATION
Coupled Solution of System and Sensitivity Equations
Frank (1978)
Tomovic (1963)
Dickinson and Gelinas (1976)
Eno and Rabitz (1979)
Tang and Pinder (1977, 1979)
Tomovic and Vucobratovic (1972)
Adjoint (Green's Function) Solution of Sensitivity Equation
Hwang et al. (1978)
Dougherty et al. (1979)
Hwang and Rabitz (1979)
Sensitivity Measures
Mean
Variance
Local Perturbation
Local Perturbation
Local Perturbation

Figure 3. Survey of local sensitivity analysis methods.

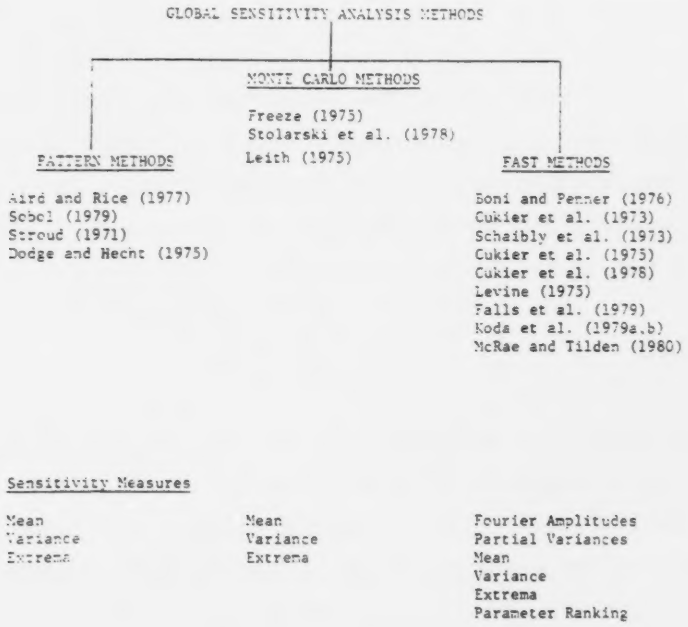
GLOBAL SENSITIVITY ANALYSIS METHODS
PATTERN METHODS
Aird and Rice (1977)
Sobol (1979)
Stroud (1971)
Dodge and Hecht (1975)
MONTE CARLO METHODS
Freeze (1975)
Stolarski et al. (1978)
Leith (1975)
FAST METHODS
Boni and Penner (1976)
Cukier et al. (1973)
Schaibly et al. (1973)
Cukier et al. (1975)
Cukier et al. (1978)
Levine (1975)
Falls et al. (1979)
Koda et al. (1979a,b)
McRae and Tilden (1980)
Sensitivity Measures
Mean
Variance
Extrema
Mean
Variance
Extrema
Fourier Amplitudes
Partial Variances
Mean
Variance
Extrema
Parameter Ranking

Figure 4. Survey of global sensitivity analysis methods.

the system being analysed. Despite the wide spread interest in sensitivity analysis one of the major barriers to the effective use of most of the techniques is the availability of general purpose software. Some programs are available notably the general purpose kinetics program of Kee et al. (1980), the FAST program of McRae et al. (1982) and the Green's function method of Kramer et al. (1982). There are at present no generally available computer codes for the systematic sensitivity analysis of large systems of coupled partial differential equations. One encouraging observation that can be made however is that the direct decoupled method, described in section 6, offers considerable potential for widespread application.

CONCLUSIONS

In this paper a number of different techniques have been described that can be used to examine the effects of parameter uncertainties on model predictions. At present while the depth of available techniques is quite large there are substantial practical barriers to their widespread use in evaluating the predictions of complex nonlinear models. One method introduced in this paper, the direct decoupled sensitivity analysis technique offers the potential for a major breakthrough, to the point where it is clearly feasible to make use of the method in long range transport studies. There is a clear need for systematic analyses of model performance. Information from such studies can provide critical insight into the dominance of particular processes and more importantly, the sensitivity results can set the focus for future research efforts.

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LIST OF SYMBOLS

$\underline{A}(\underline{u},\underline{p})$	Boundary operators $[A_1(\underline{u},\underline{p}),\ldots,A_n(\underline{u},\underline{p})]$
$\underline{B}(\underline{p},\underline{x})$	Inhomogeneous boundary operators $[B_1(\underline{p},\underline{x}),\ldots,B_n(\underline{p},\underline{x})]$
$\underline{F}[\underline{p},\underline{x}]$	A vector of inhomogeneous source terms $[F_1(\underline{p},\underline{x}),\ldots,F_n(\underline{p},\underline{x})]$
m	Number of system parameters
n	Number of state variables
$\underline{N}(\underline{u},\underline{P})$	A vector of nonlinear operators $[N_1(\underline{u},\underline{p}),\ldots,N_n(\underline{u},\underline{p})]$
$\underline{p}(\underline{x})$	A vector of the m system parameters $[p_1(\underline{x}),\ldots,p_m(\underline{x})]$
r	Number of independent variables (e.g., for $r=4$ $x=(x,y,z,t)$)
$\underline{R}(\underline{u},\underline{p})$	A vector of response functions $[R_1(\underline{u},\underline{p}),\ldots,R_s(\underline{u},\underline{p})]$
s	Number of response functions
$\underline{u}(\underline{x})$	An n dimensional state vector $= [u_1(\underline{x}),\ldots,u_n(\underline{x})]$
$\underline{x}$	A vector of independent variables $\underline{x} = [x_1,\ldots,x_r]$

REFERENCES

Aird, T.M. and J.R. Rice, 1977. Systematic Search in Higher Dimensional Sets. **SIAM J. Numerical Analysis**, 14:296-312.

Atherton, R.W., R.B. Schainker and E.R. Ducot, 1975. On the Statistical Sensitivity Analysis of Models for Chemical Kinetics. **AIChE Journal**, 21: 441-448.

Barhen, J. and D.G. Cacuci, 1980. An Efficient Procedure to Evaluate Second-Order Sensitivities for Nonlinear Problems with Nonlinear Responses. **Transactions of American Nuclear Society**, 35:266-267.

Boni, A.A. and R.C. Penner, 1976. Sensitivity Analysis of a Mechanism for Methane Oxidation Kinetics. **Combustion Science and Technology**, 15:99-105.

Cacuci, D.G.. 1981a. Sensitivity Theory for Nonlinear Systems, I. Nonlinear Functional Analysis Approach. **J. Mathematical Physics**, 22:2794-2802.

Cacuci, D.G., 1981b. Sensitivity Theory for Nonlinear Systems, II. Extensions to Additional Classes of Responses. **J. Mathematical Physics**, 22: 2803-2812.

Cacuci, D.G., P.J. Maudlin, C.V. Parks and C.F. Weber, 1981. Recent Advances and Applications of Differential Sensitivity Theory in Reactor Safety," Proceedings ANS/ENS International Topics Meeting on Advances in Mathematical Methods for Nuclear Engineering Problems, Munich, Federal Republic of Germany, April 27-29.

Cacuci, D.G., C.F. Weber, E.M. Oblow and J.H. Marable, 1980. Sensitivity Theory for General Systems of Nonlinear Equations. **Nuclear Science and Engineering**, 75:88-110.

Cope, J.E. and B.W. Rust, 1979. Bounds on the Solution of Linear Systems with Inaccurate Data. **SIAM J. Numerical Analysis**, 16:950-963.

Costanza, V. and J.H. Seinfeld, 1981. Stochastic Sensitivity Analysis in Chemical Kinetics. J. **Chemical Physics**, 74:3852-3858.

Crossley, T.R. and B. Porter, 1969. Eigenvalue and Eigenvector Sensitivities in Linear Systems Theory. **Int. J. Control**, 10:163-170.

Cukier, R.I., C.M. Fortuin, K.E. Shuler, A.G. Petschek and J.H. Schaibly, 1973. Study of the Sensitivity of Coupled Reaction Systems to Uncertainties in Rate Coefficients: I Theory. J. **Chemical Physics**, 59:3873-3878.

Cukier, R.I., H.B. Levine and K.E. Shuler, 1978. Nonlinear Sensitivity Analysis of Multiparameter Model Systems. J. **Computational Physics**, 26:1-42.

Cukier, R.I., J.H. Schaibly and K.E. Shuler, 1975. Study of the Sensitivity of Coupled Reaction Systems to Uncertainties in Rate Coefficients: III Analysis of the Approximations. J. **Chemical Physics**, 63:1140-1149.

Curtain, R.F. and A.J. Pritchard, 1977. Functional Analysis in Modern Applied Mathematics. Academic Press, London, 339 pp.

Dermilap, M. and H. Rabitz, 1981a. Chemical Kinetic Functional Sensitivity Analysis: Elementary Sensitivities. J. **Chemical Physics**, 74:3362-3375.

Dermilap, M. and H. Rabitz, 1981b. Chemical Kinetic Functional Sensitivity Analysis: Derived Sensitivities and Further Applications. J. **Chemical Physics**, 75:1810-1819.

Dickinson, R.P. and R.J. Gelinas, 1976. Sensitivity Analysis of Ordinary Differential Equation Systems--A Direct Method. J. **Computational Physics**, 21:123-143.

Dougherty, E.P., J.-T. Hwang and H. Rabitz, 1979. Further Developments and Aplications of the Green's Function Method of Sensitivity Analysis in Chemical Kinetics. J. **Chemical Physics**, 71:1794-1808.

Dougherty, E.P. and H. Rabitz, 1980. Computational Kinetics and Sensitivity Analysis of Hydrogen-Oxygen Combustion. J. **Chemical Physics**, 72: 6571-6586.

Dunker, A.M., 1980. The response of an Atmospheric Reaction Transport Model to Changes in Input Function. **Atmos. Environ.**, 14:671-679.

Dunker, A.M, 1984. The Decoupled Direct Method for Calculating Sensitivity Coefficients. Preprint of a paper to appear in J. Chemical Physics.

Edelson, D. and D.L. Allara, 1980. A Computational Analysis of the Alkane Pyrolysis Mechanism: Sensitivity Analysis of Individual Reaction Steps. Int. J. **Chemical Kinetics**, 12:605-621.

Edelson, D., L.C. Kaufman and D.D. Warner, 1981. The Use of a High-Speed Vector Processor for Chemical Kinetic Sensitivity Analysis. American Chemical Society Symposium Series, 173, Super Computers in Chemistry, eds P. Lykos and I. Shavitt, 79-88.

Falls, A.H., G.J. McRae and J.H. Seinfeld, 1979. Sensitivity and Uncertainty Analysis of Reaction Mechanisms for Photochemical Air Pollution. Int. J. **Chemical Kinetics**, 11:1137-1162.

Frank, P.M., 1978. Introduction to System Sensitivity Theory. Academic Press, New York, 386 pp.

Gelinas, R.J. and J.P. Vajk, 1978. Systematic Sensitivity Analysis of Air Quality Simulation Models. Final Report to the U.S. Environmental Protection Agency under Contract Number 68-02-2942, 96 pp.

Hwang, J.-T., 1982. Nonlinear Sensitivity Analysis in Chemical Kinetics. Proc. National Science Council, B, 6, Republic of China, 20-29.

Hwang, J.-T., E.P. Dougherty, S. Rabitz and H. Rabitz, 1978. The Green's Function Method of Sensitivity Analysis in Chemical Kinetics. J. **Chemical Physics**, 69:5180-5191.

Kato, T., 1966. Perturbation Theory for Linear Operators. Springer-Verlag, New Yor, *** pp.

Kee, R.J., J.A. Miller and T.H. Jefferson, 1980. CHEMKIN: A General Purpose, Problem-Independent, Transportable, Fortran Chemical Kinetics Code Package. Sandia Laboratories Report No. SAND80-8003, Sandia Laboratories, Albuquerque, New Mexico, 204 pp.

Kelley, H.J. and W.F. Denham, 1969. Modeling and Adjoints for Continuous Systems. **J. Optimization Theory and Applications**, **3**:174-183.

Kilkas, A.C. and H.P. Hutchison, 1980. Process Optimization Using Linear Models. **Computers and Chemical Engineering**, **4**:39-48.

Koda, M., A.H. Dogru and J.H. Seinfeld, 1979a. Sensitivity Analysis of Partial Differential Equations with Application to Reaction and Diffusion Processes. **J. Computational Physics**, **30**:259-282.

Koda, M., G.J. McRae and J.H. Seinfeld, 1979b. Automatic Sensitivity Analysis of Kinetic Mechanisms. **Int. J. Chemical Kinetics**, **11**:427-444.

Koda, M. and J.H. Seinfeld, 1982. Sensitivity Analysis of Distributed Parameter Systems. **IEEE Transactions on Automatic Control**, **AC-27**:951-955.

Kramer, M.A. and J.M. Calo, 1981. An Improved Computational Method for Sensitivity Analysis: Green's Function Method with 'AIM'. **Applied Mathematical Modelling**, **5**:432-441.

Kramer, M.A., R.J. Kee and H. Rabitz, 1982. CHEMSEN: A Computer Code for Sensitivity Analysis of Kinetic Mechanisms. Sandia Laboratories Report No. SAND82-8230, Sandia Laboratories, Albuquerque, New Mexico, 23 pp.

Kramer, M.A., H. Rabitz, J.M. Calo and R.J. Kee, 1984. Sensitivity Analysis in Chemical Kinetics: Recent Developments and Computational Comparisons. **Int. J. Chemical Kinetics**, **16**:559-578.

Leis, J.R. and M.A. Kramer, 1984. Sensitivity Analysis of Systems of Differential and Algebraic Equations. Preprint of a paper to be presented at AIChE National Meeting, San Francisco, November 25-30.

Lojek, B., 1982. Sensitivity Analysis of Nonlinear Cricuits. IEE Proceedings, 129, Part G, 85-88.

Martin, R.H., 1976. Nonlinear Operators and Differential Equations in Banach Spaces. John Wiley and Sons, New York, 440 pp.

Maudlin, P.J., C.V. Parks and D.G. Cacuci, 1981. Differential Sensitivity Theory Applied to Movement of Maximum Responses. **Transactions of American Nuclear Society, 38**:333-334.

Magnus, W., 1954. On the Exponential Solution of Differential Equations for a Linear Operator. **Communications on Pure and Applied Mathematics**, VII:649-673.

McKay, M.D., R.J. Beckman and W.J. Conover, 1979. A Comparison of Three Methods for Selecting Values of Input Variables in the Analysis of Output from a Computer Code. **Technometrics**, 21:239-245.

McRae, G.J., 1984. Sensitivity Analysis of Systems of Partial Differential Equations. (Submitted for publication).

McRae, G.J., J.W. Tilden and J.H. Seinfeld, 1982. Global Sensitivity Analysis--A Computational Implementation of the Fourier Amplitude Sensitivity Test (FAST). **Computers in Chemical Engineering**, 6:15-25.

Milford, J.B. and G.J. McRae, 1984. A Method for Sensitivity Analysis of Source-Receptor Matrices: I Application to Acid Deposition Control Strategies. (Submitted for publication).

MOI, 1982. United States-Canada Memorandum of Intent on Transboundary Air Pollution. (A series of reports on the scientific issues related to the long range transport, transformations and deposition of acidic materials). Copies of the report are available from the U.S. Environmental Protection Agency, Washington, D.C.

NCAR, 1983. Regional Acid Deposition: Models and Physical Processes. Report Number NCAR/TN-214+STR, National Center for Atmospheric Research, Boulder, Colorado.

NRC, 1983. Acid Deposition: Atmospheric Processes in Eastern North America. National Resources Council, National Academy Press, Washington, D.C.

Oblow, E.M., 1971. Sensitivity Theory for General Nonlinear Algebraic Equations with Constraints. **Nuclear Science and Engineering**, 65:187-191.

Parker, S.R., 1971. Sensitivity: Old Questions, Some New Answers. **IEEE Transactions on Circuit Theory, CT-18**:27-40.

Parks, C.V. and P.J. Maudlin, 1981. Application of Differential Sensitivity Theory to a Neutronic/Thermal-Hydraulic Reactor Safety Code. **Nuclear Technology**, **54**:38-53.

Perkins, W.R., 1971. Sensitivity Analysis. **In**: Feedback Systems, ed. J.B. Cruz, McGrall-Hill, New York, 19-65.

Pierce, T.H. and R.I. Cukier, 1981. Global Nonlinear Sensitivity Analysis Using Walsh Functions. **J. Computational Physics**, 41:427-443.

Rabitz, H., M. Kramer and D. Dacol, 1983. Sensitivity Analysis in Chemical Kinetics. **Annual Review of Physical Chemistry**, 34:419-461.

Saaty, T.L., 1981. Modern Nonlinear Equations. Dover Publications, New York, 471 pp.

Schaibly, J.H. and K.E. Shuler, 1973. Study of the Sensitivity of Coupled Reaction Systems to Uncertainties in Rate Coefficients. II Applications. **J. Chemical Physics**, 59:3879-3888.

Seigneur, C., G. Stephanopolouous and R.W. Carr, 1982. Dynamic Sensitivity Analysis of Chemical Reaction Systems--A Variational Approach. **Chemical Engineering Science**, 37:845-853.

Seigneur, C., T.W. Tesche, P.M. Roth and L.E. Reid, 1981. Sensitivity of a Complex Urban Air Quality Model to Input Data. J. **Applied Meteorology**, 20: 50-70.

Stolarski, R.S., D.M. Butler and R.D. Rundel, 1978. Uncertainty Propagation in a Stratospheric Model 2. Monte Carlo Analysis of Imprecision Due to Reaction Rates. **J. Geophysical Research**, 83:3074-3078.

Tang, D.H. and G.F. Pinder, 1977. Simulationof Ground Water Flow and Mass Transport Under Uncertainty. **Advances in Water Resources**, 1:25-30.

Tang, D.H. and G.F. Pinder, 1979. Analysis of Mass Transport with Uncertain Physical Parameters. **Water Resources Research**, 15:1147-1155.

Tapia, R.A., 1971. The Differentiation and Integration of Nonlinear Operators. In: Nonlinear Functional Analysis, L.B. Rall (Ed.), Academic Press, New York, 45-101.

Tilden, J.W., V. Costanza, G.J. McRae and J.H. Seinfeld, 1981. Modelling of Chemical Reaction Systems. **Springer-Verlay Series in Chemical Physics**, 18:69-91, Springer-Verlag, New York,

Tomovic, R., 1963. Sensitivity Analysis of Dynamic Systems. McGraw-Hill, New York, 258 pp.

Tomovic, R. and M. Vukobratovic, 1972. General Sensitivity Theory. American Elsevier Publishing Company, Inc., New York, 258 pp.

CHAPTER VI

QUANTIFYING UNCERTAINTY IN LONG RANGE TRANSPORT MODELS

SUMMARY OF RECOMMENDATIONS OF EULERIAN LONG RANGE TRANSPORT MODELING SUBGROUP

Workshop on Sources and Evaluation of
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EULERIAN LRT MODEL EXPECTATIONS

Eulerian long range transport models are designed to study the relationship between source emissions and receptor air quality over large areas. At present there are several large scale development activities directed at constructing models of the physical and chemical processes occurring in the atmosphere. Given the availability of suitable input data it is expected that these models will be able to predict:

1. Gas phase concentrations of; NO_x, SO_x, O_3, NO_2, H_2O_2, PAN, HONO, NH_3, HNO_3, hydrocarbons and CO.
2. Aqueous phase concentrations of; pH, SO_4, NO_3, NH_4, organic acids and chloride.
3. For aerosols, the only available models are simple equilibrium formulations of the sulfate-nitrate-ammonia system. A clear direction for future development activities would be to add the capability to handle particle size distributions.
4. All the chemical species are available at a horizontal resolution of approximately 100 km x 100 km. Predicted fields, over large dimensions, can be calculated by simply accumulating the gridded information.
5. The smallest time resolution of predicted concentrations is controlled by numerical integration constraints (time steps of order of 10 minutes). Comparisons of predictions against observations can be carried out by averaging the model outputs.
6. Given the gas and aqueous species, described above, it is possible to calculate both the dry and wet deposition patterns over regional scales as well as at target receptor locations.

CRITERIA AND PROCEDURES FOR QUANTIFYING ERRORS IN EULERIAN LRT MODELS

It is the opinion of the working group that the appropriate criteria and procedures for quantifying errors in Eulerian LRT models should be based on two considerations:

i. the need to demonstrate effectively the impact of alternative control strategies,

ii. the need to quantify indices of model performance over the total domain or over sub-domains representative of different meteorological processes.

The former could be semi-quantitative (relying on relative signal changes) until experience with the models permits determination of a more objective numerical criterion. The latter would make use of measures of the models precision in simulating time and space variations in model output parameters to guide in systematic improvement in process representation.

The uncertainty in model outputs comprise input uncertainty and model formulation uncertainty. The formulation uncertainty will include a component relating to the representation of the physical-chemical processes and part attributable to the mathematical integrations. Insight into the models response to arbitrarily varying inputs for a particular formulation can be studied effectively by methods currently available (see paper by McRae for details). Complete evaluation of the models demands systematic comparison with quality controlled observational data over as extensive a model domain as possible. It should be recognized that the effect of subgrid scale processes, turbulence representation in transport processes and problems of specification of input fields will result in a limit of predictability analagous to that for meteorological forecast models.

Model evaluation initially should emphasize the time and space scales simulated by the LRT models by studies of: 1) standard statistical measures of predictands previously mentioned over the total domain and over stratified data subsets; 2) time series of model-observation residuals; and 3) pattern recognition techniques.

There is a further need to establish the bias and uncertainty associated with averaging or compounding model outputs required as input to evolving environmental effects-type models.

Currently available data sets such as OSCAR and NEROS need to be studied in depth, in conjunction with improved emission inventories, to give preliminary insight into evaluation methods and to refinement of design factors of a more comprehensive evaluation data base such as length of record, numbers of replications, data stratification methods, and model parameter specification methods. Finally there is a need to examine in detail how the model performance criteria should be formulated.

DATA REQUIREMENTS FOR MODEL PERFORMANCE EVALUATION

It is beyond the scope of this workshop to discuss in detail the design basis for a monitoring program to evaluate long range transport models, though it is recommended that such an activity should be started. The working group has outlined in generic terms those meteorological and chemical measurements thought to be most important in achieving successful model performance evaluations. We have deferred any discussion on emission inventory data requirements to the Lagrangian Modeling Working Group.

A. Meteorological Measurements

The primary set of measurements should to obtained on a nested grid with varying resolution ranging on the course scale from 200 km and 6 hrs to that on the fine scale of 50 km and 2 hrs. They include:

> Ground-level precipitation
> Cloud type and spatial characteristics
> Vertical profiles of temperature, humidity, and wind
> Vertical profiles of cloud water and hydrometeor concentrations

In addition, detailed boundary layer intensive studies should be performed in concert with the basic research monitoring program to acquire highly resolved concentration and turbulence data in conjunction with relevant biological properties effecting the dry deposition of atmospheric species.

B. Chemical Measurements

Ambient measurements of a wide variety of chemical species are required to run and evaluate regional air quality and deposition models which incorporate sophisticated descriptions of the chemical transformation processes occurring in the atmosphere. In addition, information on the emission of a select number of chemical species is also required. Tables 1 and 2 provide a list of the chemical species, measurement and monitoring characteristics, and rationale for collection.

The averaging time in regional models is of the order of one to three hours which is commensurate with the models spatial resolution of 20 to 100 km. As with the meteorological data, nested monitoring networks of varying resolution will provide the necessary data to understand and develop improved techniques, if warranted, to treat subgrid scale processes. In addition, enhanced spatial resolution of the monitoring data provides the opportunity to determine the spatial representativeness of point measurements. An issue of importance not only to the performance evaluation of models, but to the empirical estimation of depositional loading itself.

EULERIAN MODEL OUTPUTS FOR LONG TIME AVERAGES

Current generation Eulerian long-range transport models by nature of their comprehensiveness and complexity are most efficient (economical) in studying episodic acid deposition events, i.e. events lasting a few days to a week. In principle given the proper continuous input data, these models can estimate seasonal or even annual averages of acid deposition directly. To do so would be very costly computationally. Several procedures have been suggested to circumvent this difficulty.

First, it is observed that most of the yearly synoptic events in a given region, for example the north-eastern United States and south-eastern Canada can be grouped into general meteorological categories. It is proposed that Eulerian long range transport models can be used to study the deposition associated with each category of synoptic event and then use the cumulative simulation data to estimate seasonal and annual averages. In

TABLE 1

REQUIRED INFORMATION ON CHEMICAL SPECIES

			Measurement Need						Frequency				
			Dry		Vertical	Phase							
Species	**Priority**	**Emission**	**Depos. Flux**	**Surface**	**Profile**	**Gas**	**Aqueous**	**Part.**	**Event**	**Long-Term**	**Run**	**Evaluate**	**Rationale for Measurement**
SO_2	1	X	X	X	X	X			X	X	X	X	Primary emission and precursor to $SO_4^=$
SO_4/ S(IV)/ S(VI)	1	X	X	X	X		X	X	X	X	X	X	Major species of concern
NO	1	X		X	X	X			X	X	X		Primary emission, precursor to NO_3^-
NO_2/ NO_3	1		X	X	X	X			X	X	X	X	" " " "
HNO_3	1		X	X	X	X	X	X	X	X		X	Major species of concern
O_3	1		X	X	X	X			X	X	X	X	Influences $SO_2 \rightarrow SO_4^=$ and NO_x NO_3^- oxidation
H_2O_2	1		X	X	X	X	X		X	X	X	X	Major oxidant for aqueous oxidation of $S(IV) \rightarrow S(VI)$
Fe, Mn	1	X		X	X			X	X		X	X	Catalyzes O_2 oxidation of $S(IV) \rightarrow S(VI)$
Soil Dust $CO_3^=$	1	X		X				X	X		X	X	Influences pH of water
NH_3	1	X	X	X	X	X			X		X	X	Influences pH of water
RHC	1	X		X	X	X			X		X	X	Participates in radical production which drives SO_2 and NO_x oxidation
HCHO	1	X		X	X	X			X		X	X	Radical initiator and also complexing agent with S(IV)
RCHO	2	X		X		X			X		X	X	Radical initiator
Carbon	2	X		X	X		X O&E		X		X		Influences aq. phase oxidation of S

TABLE 1 (Continued)

				Measurement Need									
						Phase			Frequency				
Species	Priority	Emission	Dry Depos. Flux	Surface	Vertical Profile	Gas	Aqueous	Part.	Event	Long-Term	Run	Evaluate	Rationale for Measurement
HCOOH	2	X		X	X		X		X			X	Contributes to acidity
RCOOH	2	X		X			X		X			X	Contributes to acidity
Cl^-	1			X			X	X	X			X	Contributes to acidity
	1			X			X		X		X	X	Measure of acidity of water
NH_4^+	1			X			X	X	X		X	X	Important for aq. phase chem
Biogenic HC	2	X		X		X			X		X	X	Radical initiator, important relative to man-made emissio
CH_4		X		X	X	X			X		X		Role in long range transport chemistry
CO	2	X		X	X	X			X		X	X	Tracer for air masses
PAN	1			X	X	X			X		X	X	Temporary sink for NO_x; role in photoxidation influencing O_3
HONO	2	X		X		X			X		X	X	Radical initiator; temp. NO_x sink

TABLE 2

BASIC MEASUREMENTS FOR REGIONAL GROUND NETWORK AND SOUNDINGS

Parameter	Method	Ground	Sampling Frequency	Aloft	Sampling Frequency
A. **Basic**					
Sulfur dioxide (SO_2)	Filter Pack	X	Daily, 6 hr	X	2/day, 2/week
Particulate Sulfate ($SO_4^{=}$)	Filter Pack	X	Daily, 6 hr	X	2/day, 2/week
Nigrogen Oxides (NO, NO_2)	Chemiluminescent	X	Daily, 1 hr	X	2/day, 2/week
Nitric Acid (HNO_3)	Filter Pack	X	Daily, 1 hr	X	2/day, 2/week
Ozone (O_3)	U.V. Absorption	X	Daily, 1 hr	X	2/day, 2/week
Precipitation	Tip/buck. Collector	X	Event		
Precipitation $SO_4^{=}$	Bucket Collector	X	Event		
Precipitation NO_3^{-}	Bucket Collector	X	Event		
Cloud Water (Ice)	Optical Counter		Event	X	2/day, 2/week
Cloud $SO_4^{=}$	SUNYA Collector		Event	X	2/day, 2/week
Cloud NO_3	SUNYA Collector		Event	X	2/day, 2/week
Winds	Rotating Cup & Vane (or Rawinsonde)	X	Daily, Cont.	X	(4/day)
Temperature	Thermocouple/ Thermistor	X	Daily, Cont.	X	2/day, 2/week
Hunidity	Chilled Mirror or Rawinsonde	X	Daily, Cont.	X	2/day, 2/week
Barometric Pressure or Height	Pressure Transducer	X	Daily, Cont.	X	2/day, 2/week
Turbulence	(HRI)		Daily, Cont.	X	2/day, 2/week
Light Scattering	Nephelometer		Daily, Cont.	X	2/day, 2/week

	Parameter	Method	Ground	Sampling Frequency	Aloft	Sampling Frequency
A.	**Basic** (Continued)					
	Precipitating Clouds	Doppler Radar	X	Daily, Cont.		
	Cloud Cover	(Satellite)		Daily, Cont.		
B.	**Special**					
	Particle NH_4^+	Filter Pack	X	Daily, 6 hr	X	2/day, 2/week
	Particle NO_3	Filter Pack	X	Daily, 6 hr		
	Particle Metals	Filter Pack	X	Daily, 6 hr	X	2/day, 2/week
	Precip/Cloud NH_4^+	Collector	X	Event	X	2/day, 2/week
	Precip/Cloud Metals	Collector	X	Event	X	2/day, 2/week
	Precip/Cloud H^+	Collector	X	Event	X	2/day, 2/week
	Peroxacetyl Nitrate (PAN)	GC	X	Daily, 1 hr	X	2/day, 2/week
	Hydrogen Peroxide (H_2O_2)	HRP	X	Daily, 6 hr	X	2/day, 2/week
	Reactive HC	GC	X	Daily, 6 hr	X	2/day, 2/week
	Ammonia (NH_3)	Filter Pack	X	Daily, 6 hr	X	2/day, 2/week
	Dry Flux SO_x, NO_x	Accum. Flux	X	Daily, 6 hr		
	HONO	Laser Spectometer	X	Event		
	Organic Nitrates	GC (?)	X	Event		
	HCHO	DNPH/Laser Spectrometer	X	Daily		
	RCHO	DNPH	X	Daily		
	HCOOH	IC	X	Event		
	CH_4	GC	X	Daily		

Parameter	Method	Ground	Sampling Frequency	Aloft	Sampling Frequency
B. Special (Continued)					
Cl	Filter Pack	X	Event		
Carbon	Filter Pack	X	Event		
CO	MDIR	X	Daily		

establishing the frequency of occurrences of each category of deposition event in a season and the amount and distribution of deposition, one can compute a statistical ensemble average for that season. Unfortunately, this procedure has not seen prior application in meteorology or in air pollution research on a regional scale. A feasibility study should be carried out with one or more existing data bases. Sulfate wet deposition in the eastern United States is a definite possible choice for testing the technique.

A different approach toward obtaining seasonal and annual averages would be the use of full scale Eulerian LRT to develop simpler models that are more computational efficient but less comprehensive in the inclusion of detailed physical and chemical processes. These simpler models, or "engineering models" can be either Eulerian or Lagrangian in structure. Their essential feature must be that the accuracy of their representation of the physical and chemical details can be verified by selective use of the comprehensive Eulerian LRT models. These computational efficient "engineering models" then will be used to study seasonal and annual depositions in a regional scale. It is emphasized that simulation results from these "engineering models" must be checked frequently to avoid significant deviations from the results of the comprehensive models.

UNCERTAINTIES IN EULERIAN MODEL PREDICTIONS

A large contribution to the uncertainty in Eulerian long range transport model predictions is due to the spatial and temporal limitations of the available input data. It is generally felt that model uncertainty can be reduced by increasing the spatial and temporal resolution of the input data (e.g. improvements in rawinsondes data, land use information, and emissions). However since the cost of obtaining higher density and more frequent inputs may be large, it is important to estimate how the uncertainty will decrease as the input resolution is increased. One approach to quantifying the improvement is to use existing models to study their sensitivity to input data. For example, the NCAR meteorological model is being used to investigate the sensitivity of predicted trajectories to changes in the spatial and temporal resolution of the wind field.

It is recommended that direct simulation studies, using existing models, be initiated to quantify the sensitivity of model predictions to increases in the spatial and temporal resolution of the input data.

THE FOCUS OF FUTURE RESEARCH TO REDUCE UNCERTAINTIES IN EULERIAN MODELS

The largest sources of uncertainty in current LRT Eulerian models are due to:

i. lack of data bases to initiate, run and evaluate the model and its modules
ii. incomplete formulation of processes in models

Specifications for an observational program using existing instrumentation have been outlined in a previous section of this paper. In order to improve the quality of such observations it is necessary that considerable research and development effort be directed toward improving the sensitivity, time resolution and robustness of air concentration measurement techniques especially for sulfur-aerosols, SO_2, NO_x, NH_3, PAN and reactive hydrocarbons.

Better formulations and evaluation data bases are needed for subgrid scale representativeness of the following processes:

i. transport/dispersion, removal and chemical conversion processes associated with cloud fields including the very neglected, important process of fogwater deposition.
ii. dry deposition process, in particular those related to complex terrain and heterogeneous, biologically controlled surfaces.
iii. the dispersion/transport, removal and chemical conversion of pollution released by point or area sources smaller than the grid resolution of the model.

Another model formulation that is unnecessarily incomplete is that for aerosol species, which are not distributed by particle size in current generation regional models. Since the processes of wet and dry removal and that of chemical transformation are particle size dependent, the incorporation of an aerosol growth module in the models is an important improvement for consideration.

There is insufficient information on the mechanism of air-surface exchange of many gases in the model (e.g.. hydrocarbons). It is recommended that further experimental studies as well as exercises that generalize experimental results be undertaken.

There are several research needs related to gas phase chemistry uncertainties:

1. more smog chamber studies on time scales applicable to LRT schemes,
2. investigation of nighttime chemistry of nitrogen compounds,
3. kinetic data for temperatures of 0-20°C rather than the more typical studied temperature of 25°C,
4. continued study of the role of natural hydrocarbons in the photochemical process.

It is recommended that methods for obtaining seasonal or annual mean concentration fields, deposition fields and source-receptor transfer matrices be investigated. Two possibilities are:

1. to use the comprehensive Eulerian model to obtain simple, accurate parameterizations of processes that can be used in faster Eulerian or Lagrangian models to generate long-term average outputs (e.g. proposal by Prahm),
2. to study the feasibility of stratifying meteorological synoptic classes, from which analysis of a fraction of representative classes can be used to reconstruct seasonal or annual means (e.g. proposal by NCAR).

Another important task related to transport mechanisms is to improve four dimensional data assimilation procedures. A large part of the uncertainty in the transport/diffusion calculation in an LRT model is due to the lack of meteorological information on the mesoscale. Fundamentally, there is a lack of mesoscale data, but to a considerable extent the gaps can be filled through the use of a mesoscale meteorological model incorporating a good boundary layer treatment. The assimilation and initialization must be done in such a way as to incorporate the synoptic scale information present in the data and at the same time preserve the smaller scale structure produced by the model.

CHAPTER VII

QUANTIFYING UNCERTAINTY IN LONG RANGE TRANSPORT MODELS

SUMMARY OF RECOMMENDATIONS OF LAGRANGIAN LONG RANGE TRANSPORT MODELING SUBGROUP

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USES AND LIMITATIONS OF LAGRANGIAN LONG RANGE TRANSPORT MODELS

Lagrangian long range transport (LLRT) models have been used widely both to diagnose source-receptor relationships for atmospheric sulfur oxide concentrations and sulfur deposition and to estimate the potential changes in sulfur concentration and deposition values following changes in the emissions distribution of sulfur dioxide. Similarly, some LLRT models have also been used to calculate the concentrations and deposition of nitrogen compounds. In general the LLRT models are popular because:

1) they are simple in concept, and hence generally inexpensive to operate, and
2) they are presently operational.

Several reviews of LLRT models have been published (Bass, 1980; Eliassen, 1980; Johnson, 1981; Fisher, 1983). The reader is referred to these articles for summaries of the methodologies used in LLRT models. The purpose of this document is to summarize the present ability of LLRT models to reproduce observed concentrations of sulfur species in the atmosphere and in precipitation and to make recommendations for improvements in Lagrangian models which could increase their accuracy and reliability.

Lagrangian long range transport models have demonstrated an ability to reproduce long-term (annual) SO_2 and particulate $SO_4^=$ concentrations which are in reasonable agreement with observations. The least complicated of the LLRT models, the so-called Semi-Empirical models, have been shown to reproduce annual $SO_4^=$ concentrations to within a factor of two both in the United States (Venkatram et al., 1982) and in Europe (Fisher and Clark, 1984). Likewise the more deterministic LLRT models have also been successful in reproducing observed annual average $SO_4^=$ concentrations. Eliassen and Saltbones (1983) in Europe and Shannon (1981) in North America have shown skill in predicting particulate $SO_4^=$ concentrations. Figure 1 shows the station-by-station comparison of predicted versus observed two-year averaged $SO_4^=$ concentrations presented by Eliassen and Saltbones (1983).

There is also a statistically significant, albeit less satisfactory agreement, between calculated and observed weighted- mean annual average concentrations of $SO_4^=$ in precipitation. The reduction in accuracy in

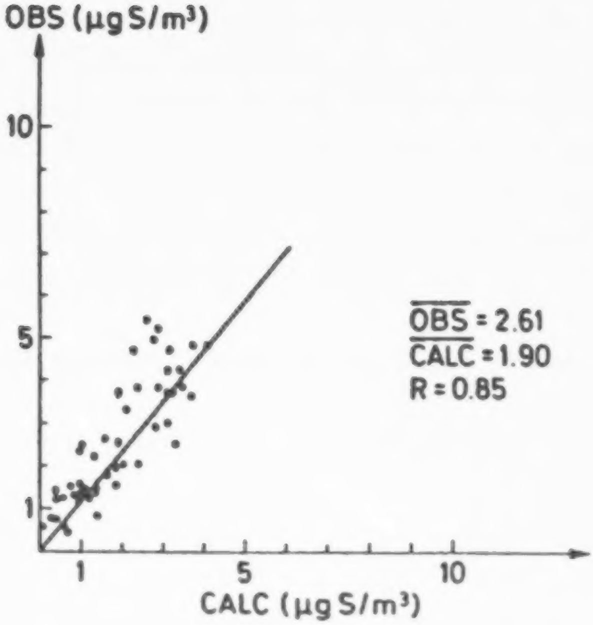

Figure 1. Observed versus calculated two-year averaged concentrations of ambient sulfate concentrations at 33 measurement sites in Europe as reported by Eliassen and Saltbones (1983).

predicting the sulfur wet deposition must be viewed relative to the accuracy of sulfur wet deposition measurements. In order to assess the degree of uncertainty in model predictions of concentrations and deposition Fox (1984) has concluded that it is necessary to study the variance of the observations in relation to the variance of the residuals (differences between observation and prediction). Voldner and Shannon (1983) predicted the annual wet deposition of sulfur in eastern Canada within the uncertainty of the observations. Eliassen and Saltbones (1983) predicted the two-year average sulfate concentration in precipitation at 33 sites with a correlation coefficient of 0.70 as compared to a correlation coefficient of 0.85 for ambient sulfate. The reduction performance is improved and regimes during which it is poor. While pairwise agreement between predicted and observed concentrations does not in itself guarantee reliable estimates of source-receptor relationships, it does give us more confidence in defining such relationships when the agreement is high. Voldner, et al. (1981), Bhumralkar, et al. (1981), and Samson and Small (1984), have demonstrated the ability of the models to reproduce frequency distributions of $SO_4^=$ concentrations. The pairwise correlation of predicted and observed daily $SO_4^=$ has been reasonably high in some studies (e.g., Voldner et al., 1981; Eliassen and Saltbones, 1983; Samson et al., 1982) but poor in others (Ruff et al., 1984). In one model evaluation, a Lagrangian long range transport model demonstrated more skill in simulating temporal variability than in simulating the fine detail of spatial concentration distributions (McNaughton et al., 1981).

The LLRT models have not demonstrated an ability to reproduce sulfur wet deposition fields on a daily or event basis as yet with much confidence. This is probably due in part to the oversimplification of pollutant scavenging processes in the models but more basic problems exist which limit our ability to ascertain specific reasons for the poor performance. The episodic behavior of precipitation events, the fact that the two-dimensional trajectories computed for precipitation events may have limited reliability in the vicinity of fronts, and our incomplete knowledge of scavenging processes undoubtedly limit the accuracy of the models' predictions of short-term sulfate deposition.

There are actually few essential differences between Lagrangian and Eulerian long range transport models apart from the frame of reference with which the flow is treated. The simplicity of LLRT models forces trade-offs which limit their resolution relative to Eulerian long range transport (ELRT) models. The specification of non-linear chemical reactions, for example, is possible with a LLRT model, but the implied horizontal mixing of the LLRT model limits the resolution of impact from specific source regions. Likewise, vertical resolution of concentration fields is more easily obtained through ELRT modeling techniques. If the Lagrangian models are reformulated to include all major effects of stratification within the air parcel, the advantages associated with their simple and elegant basic formulation is quickly lost and replaced by prohibitive complexity. This implied rapid vertical mixing in LLRT models influences the calculation of mass flux of material to the surface through dry deposition.

The description of horizontal dispersion due to vertical wind velocity shear over long time scales is intrinsically ignored in LLRT models. Samson (1980) described an uncertainty field about the mean flow resulting from the average affect of velocity shear on trajectory location, but rapid horizontal mixing of the air within the domain of this field is nonetheless presumed. Heffter (1983) has developed a branching trajectory model which splits trajectories in response to noctural deformation of the daytime transport layer.

Eliassen et al. (1982) and Rodhe et al. (1981) have demonstrated that non-linear atmospheric chemical processes can be included in receptor-oriented LLRT models, but this assumes that the rate horizontal mixing of air into the Lagrangian column or puff is known and that the boundary conditions for each species carried is known.

RECOMMENDATIONS FOR IMPROVEMENT IN LAGRANGIAN LONG RANGE TRANSPORT MODELS

There are many possibilities for improvement in LLRT models. It should be noted that most of the recommendations made below for LLRT models are equally relevant for long range transport models employing a Eulerian framework. In order of decreasing priority these improvements should involve:

1. Improved Input Data
2. More Realistic Parameterization of Scavenging Processes
3. More Realistic Representation of Chemical Transformation Processes
4. More Detail on Non-Homogeneous Nature of Dry Deposition
5. Inclusion of Cloud Venting

Each of these factors is discussed more thoroughly in the following sections.

A. Improved Input Data

It was the general consensus of the United States/Canada Memorandum of Intent (US/Canada MOI, 1983) modeling subgroup that part of the differences between the eight model results was the result of different processing of the meteorological input data and the quality of that data. Future improvements in the ability of LLRT models to reproduce observed concentration and deposition fields could depend in a large part upon more detailed and quality assured data bases.

Specifically, the data bases which would need to be improved were:

1. Emissions
2. Precipitation
3. Cloud Cover
4. Wind Field
5. Those Related to Deposition Velocities (such as land use and atmospheric stability), and
6. Other Pollutants

These will be discussed individually below.

The ability of LLRT models to predict daily and/or event concentration and deposition values is linked to knowledge of the daily fluctuations in emissions rate for SO_2. The daily emission values for the largest sources in eastern North America should be collected and archived along with an analysis of monthly mean diurnal and weekday/weekend emission patterns. Non-linear chemical transformation processes require information about the emissions of nitrogen oxides, reactive hydrocarbons, and ammonia. This emission information should be obtained on an annual basis at first with analysis of their monthly and weekday/weekend variations.

The ability of LLRT models to reproduce sulfur wet deposition values is primarily a function of the model input to reproduce the amount and type of precipitation occurring at the receptor and along the trajectory. Keeler et al., (1984) demonstrated that the ability of a LLRT model to reproduce sulfur wet deposition was limited by the accuracy of the precipitation input data. The methods used to grid precipitation data, particularly in data-sparse regions, should be evaluated for representativeness. McNaughton (1984a) has demonstrated the problems involved in preparing hourly grids of precipitation even in relatively data-rich areas and how mis-specification of the precipitation inputs can account for errors in wet deposition estimates (McNaughton, 1984c).

Information on cloud type, cloud thickness, cloud base height and percent coverage along the trajectory will be useful to the improved parameterization of several processes in long range transport modeling including heat flux estimation (for aerodynamic resistance calculations), aqueous-phase chemical transformation and wet scavenging. Although cloud data bases do exist with reasonable spatial and temporal resolution (e.g., Fey, 1978), enormous data processing will be required to use this information. A second choice for LLRT models will be to use meteorologically stratified climatologies of cloud occurrence.

The wind field information currently used in most LLRT models is derived from twice-daily upper-air observations made by synoptic networks. It is recognized that an improvement may be possible through the use of numerical weather prediction (NWP) model wind field outputs. Kuo et al. (1984) have illustrated the potential usefulness of using NWP predictions, showing an increase in trajectory accuracy using NWP analyzed winds versus normal, every 12 hour observations. The NWP model would, in effect, be used as a sophisticated temporal and spatial interpolation methodology for winds and thermodynamic properties which would be mass-consistent and dynamically correct, more reliable in data sparse areas, and, potentially, more descriptive of phenomena such as the nocturnal jet.

It is recommended to improve LLRT model predictions of dry deposition pro wind field outputs. Kuo et al. (1984) have illustrated the potential usefulness of using NWP predictions, showing an increase in trajectory accuracy using NWP analyzed winds versus normal, every 12 hour observations. The NWP model would, in effect, be used as a sophisticated temporal and spatial interpolation methodology for winds and thermodynamic properties which would be mass-consistent and dynamically correct, more reliable in data sparse areas, and, potentially, more descriptive of phenomena such as the nocturnal jet.

B. More Realistic Parameterization of Scavenging Processes

Better realization of the scavenging rates for SO_2 and $SO_4^=$ in LLRT models may be gained through better parameterization of the ensemble cloud physics and chemistry associated with entrainment, nucleation, and cloud droplet solubility. Such parameterizations may be based on a priori assumptions of the scavenging process or may be linked to estimates of the environment of other pollutants in the interstitial air of the clouds. Barrie (1981), for example, has suggested that the SO_2 washout ratio could be described as a function of rain water pH and temperature. It may also be possible to describe the scavenging of SO_2 as a function of cloud water hydrogen peroxide (H_2O_2) whose concentration could itself be parameterized as a function of cloud type, latitude, season and/or other atmospheric parameters.

It is important that the parameterization of scavenging, when based on extrapolation of theory, be reviewed for consistency with the original theory. McNaughton (1984b) has illustrated common overextension of the original theory of Scott (1978) in some current Lagrangian long range transport models.

C. More Realistic Representation of Chemical Transformation Processes

More realistic representation of both gas-phase and aqueous-phase chemical transformation processes will yield more confidence in the use of LLRT models for predicting concentration and deposition changes resulting from changing emissions patterns. The chemical mechanisms which will be used in LLRT models will necessarily be highly parameterized, reflecting the essence of chemical interrelationships gleaned from the development of more sophisticated chemical modules for ELRT models.

Aqueous-phase transformation will require more information on cloud type, depth, base height and percent cover than is presently used in LLRT models. There will also need to be a coupling of the gas-phase and aqueous-phase processes through some explicit assumption concerning the cloud entrainment rates.

Gas-phase chemistry will also require some knowledge of the cloud field in order to estimate the amount of sunlight available along the course of the trajectories for photochemistry.

D. More Detail on Non-Homogeneous Nature of Dry Deposition

For transport over long distances, it becomes very important to know the deposition velocities for the various species accurately. Sophisticated parameterization of the process require considerable detail in atmospheric and surface resistances to uptake of the species. While the atmospheric resistance can be estimated reasonably well, field experiments show that the surface resistance for important gases such as SO_2 and O_3 exhibit a large, surface-specific variation. For many other gases and particles, existing information is insufficient.

Improvements in the description of aerodynamic resistance in Lagrangian modeling are also possible. This improvement may be accomplished through a parameterization of the heat flux using time-of-day and cloud cover as surrogates for solar intensity measurements. A critical research area for many Lagrangian modelers will be the development of simple deposition parameterizations that are consistent with more sophisticated treatments.

E. Inclusion of Cloud Venting

It is estimated that, in certain circumstances, convective activity will be sufficient to redistribute pollutants from the mixed layer to a higher elevation. LLRT models could better represent surface concentrations of pollutants if upwind venting were included. Unfortunately, LLRT models are inadequate for reentraining vented air into the mixed-layer on subsequent days without assuming the vented material to be spatially homogeneous.

LLRT MODEL UNCERTAINTY AND THE USER

In order to assess the uncertainty in models and enhance the credibility in model predictions, it is essential that model results are compared with network data. For a meaningful inter-comparison between predicted and observed quantities it is necessary that the errors and uncertainties in the observations are quantified. In addition, one should carefully consider the statistical measures to be used and how to interpret subsequent results. The International Sulfur Deposition Model Evaluation (IDME) co-sponsored by Environment Canada and the U.S. Environmental Protection Agency (Clark et al., 1984)is one step in this direction. Seasonal and annual wet deposition amounts for 1980 predicted by several European and North American long range transport models are to be statistically compared with deposition amounts estimated from networks in eastern North America. Uncertainties in observations (Voldner et al., 1984), meteorological data and emissions inventories will be considered in the evaluation. One of the anticipated products of this project will be an independent error analysis of the model results which will help identify systematic problems in model formulations. In time, data from Europe, nitrate wet deposition data, and ambient air quality data will also be used in model evaluations.

One of the principal uses of the LLRT is the establishment of source-receptor relationships. Thus, it would also be desirable to evaluate the ability of models to reproduce these relationships. Unfortunately, there is little data for this purpose. Presently, the ability of a model to reproduce source-receptor relationships is circumstantial, based on the ability to reproduce observed concentration patterns. Future field studies are needed (1) to evaluate our ability to reproduce the trajectory of the winds through use of passive, non-reactive tracers and (2) to evaluate the parameterizations of deposition with tracers which emulate the pollutants of interest.

Lagrangian long range transport models represent reasonable approximations to complex atmospheric processes. The user of model predictions must, however, keep in mind the spatial limitations imposed by the LLRT framework. Attempts to apply LLRT models to near-field deposition or to situations where vertical stratification of pollutants occurs exceed the capability of these models. Further, the application of these models with linear chemical transformation to future emission scenarios must also be performed cautiously until more complete chemical mechanisms can be incorporated and tested.

REFERENCES

Bass, A., 1980. Modeling long range transport and diffusion. **In:** Proc. Second Joint Conf. on Applications of Air Pollution Meteorology, New Orleans, March 24-27, 1980, Amer. Meteor. Soc., Boston, MA, 193-215.

Barrie, L.A., 1981. The prediction of rain acidity and SO_2 scavenging in eastern North America. **Atmos. Environ.**, **15**:31-42.

Bhumralker, C.M., R.L. Mancuso, D.E. Wolf, W.B. Johnson and J. Prankath, 1981. Regional air pollution model for calculating short-term (daily) patterns and transfrontier exchanges of airborne sulfur in Europe. **Tellus**, 33:142-161.

Clark, T.L., C. Benkovitz, E.C. Voldner and M.P.Olson, 1984. The International Sulfur Deposition Model Evaluation: Phase I, 1980 North American Evaluation, Vol. 1, Standard Sulfur Deposition Model Input Data. Interim Report, Environmental Protection Agency, Research Triangle Park, NC.

Eliassen, 1980. A review of long range transport modeling. J. **Appl. Meteor.**, **19**:231-240.

Eliassen, A. and J. Saltbones, 1983. Modelling of long range transport of sulphur over Europe: A two-year model run and some model experiments. **Atmos. Environ.**, **17**:1457-1473.

Eliassen, A., Ø. Hov, I.S.A. Isaksen, J. Saltbones and F. Stordal, 1982. A Lagrangian long range transport model with atmospheric boundary layer chemistry. J. **Appl. Meteor.**, 21:1645-1661.

Fey, F.K., 1978. **The AFGWC Automated Cloud Analysis Model**. AFQWC Tech. Memo. 78-002, Offutt Air Force Base, NB, 109 pp.

Fisher, B.E.A, 1983. A review of the process and models of long range transport of air pollutants. **Atmos. Environ.**, **17**: 1865-1880.

Fisher, B.E.A. and P.A. Clark, 1984. Testing a statistical long- range transport model on European and North American observations. In: Air Pollution Modeling and its Application, Vol. 5, C. DeWispelaere, (Ed.), Plenum Press, NY (in press).

Fox, D.G., 1984. Uncertainty in air quality modeling. **Bull. Amer. Meteor. Soc., 65**:27-36.

Heffter, J.L, 1983. Branching Atmospheric Trajectory (BAT) Model. NOAA Tech. Memo. ERL ARL-121, Air Resources Laboratory, Silver Spring, MD, 19 pp.

Johnson, W.B., 1981. Interregional exchanges of air pollution: Model types and applications. **In**: Air Pollution Modeling and Its Application, Vol. 1, C. DeWispelaere, (Ed.), Plenum Press, 3-41.

Keeler, G.J., P.J. Samson and M.J. Small, 1984. Representativeness of precipitatin data in regional-scale acid deposition modeling. **In**: The Meteorology of Acid Deposition, Perry J. Samson, (Ed.), Air Pollution Control Assoc., Pittsburgh, PA, 225-240.

Kuo, Y.-H., M. Skumanich, P.L. Haagenson, and J.S. Chang, 1984. The accuracy of air parcel trajectories as revealed by observing system simulation experiments. Proc. Fourth Joint Conf. Applications of Air Poll. Meteor., Oct. 16-19, 1984, Portland, OR, Amer. Meteor. Soc., Boston, MA, 170-173.

McNaughton, D.J., C. Berkowitz and R. Williams, 1981. A diagnostic analysis of a long-term regional air pollutant transport model. **J. Appl. Meteor.**, 20:795-801.

McNaughton, D.J., 1984a. Use of currently available precipitation data for regional air quality modeling. **J. Air Poll. Cont. Assoc.**, **34**:250-252.

McNaughton, D.J., 1984b. A second look at a theoretical approach for sulfate aerosol scavenging. **In**: The Meteorology of Acid Deposition, Perry J. Samson, (Ed.), Air Pollution Control Assoc., Pittsburgh, PA, 483-495.

McNaughton, D.J., 1984c. Evaluation of wet deposition calculations in three regional air pollutant transport models. Proc. Fourth Joint Conf. Applications of Air Poll. Meteor., Oct. 16-19, 1984, Portland, OR, Amer. Meteor. Soc., Boston, MA, 228-231.

Rodhe, H., P. Crutzen and A. Vanderpol, 1981. Formation of sulfuric and nitric acid in the atmosphere during long range transport. **Tellus.**, **33**:132-141.

Ruff, R.E., K.C. Nitz, F.L. Ludwig, C.M. Bhumralkar, J.D. Shannon, C.M. Sheih, I.Y. Lee, R. Kumar, and D.J. McNaughton, 1984. **Regional Air Quality Model Assessment and Evaluation**. EPRI Report EA-3671, Electric Power Research Institute, Palo Alto, CA.

Samson, P.J., 1980. Trajectory analysis of summertime sulfate concentration in the northeastern United States. **J. Appl. Meteor.**, **19**:1382-1394.

Samson, P.J. and M.J. Small, 1984. Atmospheric trajectory models for diagnosing the sources of acid precipitation. **In:** Modeling of Total Acid Precipitation Impacts, J.L. Schnoor, (Ed.), Butterworth Publ., Boston, 1-24.

Scott, B.C., 1978. Parameterization of sulfate removal by precipitation. **J. Appl. Meteor.**, **17**:1375-1389.

Sirois, A. and E.C. Voldner, 1984. **Estimation of dry deposition velocities in North America, Part 1: The land-use data bank**. Canadian Meteor. Research Reports, CMRR 1/84, Environment Canada, Atmospheric Environment Service, Downsview, Ontario, M3H 5T4.

U.S./Canada Memorandum of Intent on Transboundary Air Pollution, 1983. **Atmospheric Sciences and Analysis Work Group 2 Phase III Final Report**, U.S. Environmental Protection Agency, Washington, D.C.

Venkatram, A., B.E. Ley and S.Y. Weng, 1982. A statistical model to estimate long-term concentrations of pollutants associated with long range transport. **Atmos. Environ.**, **16**:249-257.

Voldner, E.C. and J.D. Shannon, 1983. Evaluation of predicted wet deposition fields of sulfur in eastern Canada. **In:** The Meteorology of Acid Deposition, Perry J. Samson, (Ed.), Air Pollution Control Assoc., Pittsburgh, PA, 387-399.

Voldner, E.C., M.P. Olson, K. Oikawa and M. Loiselle, 1981. Comparison between measured and computed concentrations of sulphur compounds in eastern North America. **J. Geophys. Res.**, **86**:5339-5346.

Voldner, E.C., A. Sirois and T.L. Clark, 1984. Data screening and calculation procedures for the North American precipitation chemistry data to be used in the International Sulfur Deposition Model Evaluation. Proc. APCA Joint Specialty Conf. on Quality Assurance in Air Pollution Measurements, Boulder, CO, October, 1984.

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